

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
6 October 2005 (06.10.2005)

PCT

(10) International Publication Number
WO 2005/093109 A1

(51) International Patent Classification⁷: C22C 14/00,
C22F 1/18

(21) International Application Number:
PCT/US2005/000782

(22) International Filing Date: 7 January 2005 (07.01.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/755, 085 8 January 2004 (08.01.2004) US

(71) Applicant (for all designated States except US): MEMRY
CORPORATION [US/US]; 3 Berkshire Boulevard,
Bethel, CT 06801 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): WU, Ming, H.
[US/US]; 4 Empire Lane, Bethel, CT 06801 (US).

(74) Agent: RODRIGUES, David, E.; Cantor Colburn LLP,
55 Griffin Road South, Bloomfield, CT 06002 (US).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
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PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ,
TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA,
ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO,
SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR MANUFACTURING SUPERELASTIC β TITANIUM ARTICLES AND THE ARTICLES DERIVED THEREFROM

(57) Abstract: An article is manufactured from a composition comprising about 8 to about 10 wt% molybdenum, about 2.8 to about 6 wt% aluminum, up to about 2 wt% chromium, up to about 2 wt% vanadium, up to about 4 wt% niobium, with the balance being titanium, wherein the weight percents are based on the total weight of the alloy composition. An article is manufactured by a method comprising forming a shape from a composition comprising about 8 to about 10 wt% molybdenum, about 2.8 to about 6 wt% aluminum, up to about 2 wt% chromium, up to about 2 wt% vanadium up to about 4 wt% nobium, with the balance being titanium, wherein the weight percents are based on the total weight of the alloy composition; cold working the shape; and heat treating the shape.

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METHOD FOR MANUFACTURING SUPERELASTIC β TITANIUM ARTICLES AND THE ARTICLES DERIVED THEREFROM

BACKGROUND

[0001] This disclosure relates to superelastic β titanium alloys, methods for manufacturing these alloys and articles derived therefrom.

[0002] Alloys that undergo a martensitic transformation may exhibit a “shape memory effect”. As a result of this transformation, the high temperature phase known as “austenite” changes its crystalline structure through a diffusion-less shear process adopting a less symmetrical structure called ‘martensite’. This process may be reversible as in shape memory alloys and therefore upon heating, the reverse transformation occurs. The starting temperature of the cooling or martensitic transformation is generally referred to as the M_s temperature and the finishing temperature is referred to as the M_f temperature. The starting and finishing temperatures of the reverse or austenitic transformation are referred to as A_s and A_f respectively.

[0003] At temperatures below the A_f , alloys undergoing a reversible martensitic phase transformation may be deformed in their high temperature austenitic phase through a stress-induced martensitic transformation as well as in their low temperature martensitic phase. These alloys generally recover their original shapes upon heating above the A_f temperature and are therefore called “shape memory alloys”. At temperatures above the A_f , the stress-induced martensite is not stable and will revert back to austenite upon the release of deformation. The strain recovery associated with the reversion of stress-induced martensite back to austenite is generally referred to as “pseudoelasticity” or “superelasticity” as defined in ASTM F2005, Standard Terminology for Nickel-Titanium Shape Memory Alloys. The two terms are used interchangeably to describe the ability of shape memory alloys to elastically recover large deformations without a significant amount of plasticity due to the mechanically induced crystalline phase change.

[0004] Nitinol is a shape memory alloy comprising a near-stoichiometric amount of nickel and titanium. When deforming pseudoelastic nitinol, the formation of stress-induced-martensite allows the strain of the alloy to increase at a relatively constant stress. Upon unloading, the reversion of the martensite back to austenite occurs at a constant, but different, stress. A typical stress-strain curve of pseudoelastic nitinol therefore exhibits both loading and unloading stress plateaus. However, since the stresses are different, these plateaus are not identical, which is indicative of the development of mechanical hysteresis in the nitinol. Deformations of about 8 to about 10% can thus be recovered in the pseudoelastic nitinol. Cold worked Nitinol also exhibits extended linear elasticity. Nitinol compositions, which display linear elasticity do not display any plateau but can recover a strain of up to 3.5%. This behavior is generally termed "Linear Superelasticity" to differentiate from transformation induced "Pseudoelasticity" or "Superelasticity". These properties generally make nitinol a widely used material in a number of applications, such as medical stents, guide wires, surgical devices, orthodontic appliances, cellular phone antenna wires as well as frames and other components for eye wear. However, nitinol is difficult to fabricate by forming and/or welding, which makes the manufacturing of articles from it expensive and time-consuming. Additionally, users of nickel containing products are sometimes allergic to nickel.

SUMMARY

[0005] In one embodiment, an article is manufactured from a composition comprising about 8 to about 10 wt% molybdenum, about 2.8 to about 6 wt% aluminum, up to about 2 wt% chromium, up to about 2 wt% vanadium, up to about 4 wt% niobium, with the balance being titanium, wherein the weight percents are based on the total weight of the alloy composition.

[0006] In another embodiment, an article manufactured from a composition comprises about 8.9 wt% molybdenum, about 3.03 wt% aluminum, about 1.95 wt% vanadium, about 3.86 wt% niobium, with the balance being titanium.

[0007] In yet another embodiment, an article manufactured from a composition comprises about 9.34 wt% molybdenum, about 3.01 wt% aluminum, about 1.95 wt% vanadium, about 3.79 wt% niobium, with the balance being titanium.

[0008] In yet another embodiment, an article is manufactured by a method comprising forming a shape from a composition comprising about 8 to about 10 wt% molybdenum, about 2.8 to about 6 wt% aluminum, up to about 2 wt% chromium, up to about 2 wt% vanadium, up to about 4 wt% niobium, with the balance being titanium, wherein the weight percents are based on the total weight of the alloy composition; cold working the shape; and heat treating the shape.

[0009] In yet another embodiment, an article is manufactured by a method comprising swaging a wire having a composition comprising about 8 to about 10 wt% molybdenum, about 2.8 to about 6 wt% aluminum, up to about 2 wt% chromium, up to about 2 wt% vanadium, up to about 4 wt% niobium, with the balance being titanium, wherein the weight percents are based on the total weight of the alloy composition; cold working the shape; and heat treating the shape.

[0010] In yet another embodiment, the article manufactured from a β titanium alloy may be an eyewear frame and components, face inserts and golf club heads, orthodontic arch wires, dental implants, medical stents, filters, baskets, surgical instruments, orthopedic prostheses, orthopedic fracture fixation devices, spinal fusion and scoliosis correction devices or a catheter introducer (guide wire) and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 represents an isometric view of the eyewear frame 100;

[0012] Figure 2 represents a schematic of one possible construction of the temple 130;

[0013] Figure 3A is a front, side and bottom view of a beveled edge insert for a golf club;

[0014] Figure 3B is a bottom view of a tongue and groove edge insert for a golf club;

[0015] Figure 4A is a front view of a club face with an insert;

[0016] Figure 4B is a bottom view of Figure 4A showing the cut-out profile for the insert;

[0017] Figure 5 is a front view of a golf club face with an insert;

[0018] Figure 6A-D is a schematic representation of one method of assembling the golf club;

[0019] Figure 7 is a graphical representation showing the effect of molybdenum content on elastic recovery;

[0020] Figure 8 is a graphical representation of the effect of aging at 350°C on the elastic recovery of Sample 4 from Table 1;

[0021] Figure 9 is a graphical representation of the effect of aging at 350°C on the elastic recovery of Sample 5 from Table 1;

[0022] Figure 10 is a graphical representation showing the effect of aging at 350°C on the elastic recovery of Sample 6 from Table 1;

[0023] Figure 11 is a graphic representation showing the effect of aging at about 250 to about 550°C for 10 seconds on the elastic recovery of Sample 4 from Table 1;

[0024] Figure 12 is a graphic representation showing the effect of aging at about 250 to about 550°C for 10 seconds on the elastic recovery of Sample 5 from Table 1;

[0025] Figure 13 is a graphical representation showing the effect of cumulative cold drawing reduction on the UTS of Sample 11 from Table 2;

[0026] Figure 14 is a graphical representation showing the effect of cumulative cold drawing reduction on the Young's Modulus of Sample 11 from Table 2;

[0027] Figure 15 is a graphical representation showing the effect of tensile stress-strain curve for a wire having the composition of Sample 11 from Table 2 with 19.4% drawing reduction, tested to 2% strain;

[0028] Figure 16 is a graphical representation showing the effect of tensile stress-strain curve for a wire having the composition of Sample 11 from Table 2 with 19.4% drawing reduction, tested to 4% strain;

[0029] Figure 17 is an optical micrograph showing the microstructure of a cold drawn wire having the composition of Sample 10 from Table 2 with a 14% reduction;

[0030] Figure 18 is an optical micrograph showing partially recrystallized microstructure of a cold-drawn wire having the composition of Sample 10 from Table 2 having a 14% reduction after heat- treating at 816°C for 30 minutes;

[0031] Figure 19 is an optical micrograph showing fully recrystallized microstructure of a cold-drawn wire having the composition of Sample 10 from Table 2 having a 14% reduction after heat- treating at 871°C for 30 minutes;

[0032] Figure 20 is an optical micrograph showing the microstructure of a betatized Sample 10 from Table 2 after aging at 816°C for 30 minutes;

[0033] Figure 21 is an optical micrograph showing the microstructure of a betatized Sample 10 from Table 2 after aging at 788°C for 30 minutes;

[0034] Figure 22 is a graphical representation showing the UTS of betatized Sample 10 from Table 2 after aging at 500-900°C for 30 minutes;

[0035] Figure 23 is a graphical representation showing the ductility of betatized Sample 10 from Table 2 after aging at 500-900°C for 30 minutes;

[0036] Figure 24 is a graphical representation showing a tensile stress-strain curve tested to 4% tensile strain of a wire having the composition of Sample 11 from Table 2 after strand annealing at 871°C; and

[0037] Figure 25 is an optical micrograph showing the microstructure of a wire having the composition of Sample 11 from Table 2 after strand annealing at 871°C.

[0038] Figure 26 is a schematic of a stent;

[0039] Figure 27 represents a schematic of a perspective view of a catheter and needle assembly;

[0040] Figure 28 represents an exploded schematic of a perspective view of the catheter assembly and needle assembly including the needle tip protector;

[0041] Figure 29 is a partially exploded view of the bone reduction and fixation device showing a driver and cannulated, internally and externally threaded bone screw;

[0042] Figure 30 is a side elevational view of the bone reduction and fixation assembly of Figure 29;

[0043] Figure 31 is a cross-sectional view of the bone reduction and fixation assembly of Figure 30;

[0044] Figure 32 depicts the plan of one configuration of an arch wire;

[0045] Figure 33 depicts an enlarged side view on line 2-2 of Figure 32; and

[0046] Figure 34 depicts a plan of an arch wire with lingually positioned orthodontic brackets;

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0047] Disclosed herein are articles manufactured from β titanium alloys such as eyewear frames and frame components, face inserts and heads for golf clubs, orthodontic arch wires, dental implants, orthopedic prostheses, orthopedic fracture fixation devices, spinal fusion and scoliosis correction instruments, medical stents, filters, baskets, a catheter introducer (guide wire) and the like. The β titanium alloy exhibits pseudo-elasticity as well as linear superelasticity and may advantageously be welded, brazed, or soldered to other metals or alloys. The articles manufactured from the β titanium alloy can also be deformed into various shapes at ambient temperature and generally retain the high spring back characteristics associated with superelasticity. It is to be noted that all ranges disclosed herein are inclusive and combinable.

[0048] Pure titanium has an isomorphous transformation temperature at 882°C. The body centered cubic (bcc) structure, which is called β -titanium, is stable above the isomorphous transformation temperature and the hexagonal close packed (hcp) structure, which is called α titanium is generally stable below this temperature. When titanium is alloyed with elements such as vanadium, molybdenum, and/or niobium, the resulting alloys have an increased β phase stability at temperatures less than or equal to about 882°C (β transus temperature). On the other hand, when alloyed with elements such as aluminum or oxygen, the temperature range of the stable α phase is increased above the isomorphous transformation temperature. Elements which have the effect of increasing the β phase temperature range are called the β stabilizers, while those capable of extending the α phase temperature range are called the α stabilizers.

[0049] Unalloyed titanium transforms allotropically from body-center-cubic (bcc) β phase to hexagonal-close-packed (hcp) α phase upon cooling through the β transus temperature of 882°C. Depending on the alloying composition and thermo-mechanical processing, the ultimate microstructure of titanium alloys may have α , $\alpha+\beta$, or β phases. The so-called β alloys contain critical amounts of β -stabilizing elements and exhibit extended β stability at high temperatures and a reduction in β transus temperature to lower temperatures as elemental concentration increases. When a certain concentration level is achieved, the β phase can be retained upon rapid cooling from the beta phase field, although it is metastable. The metastable β titanium alloys may undergo lattice transformations such as martensitic transformation under applied stress. Hence, titanium alloys at critical range of β stability may exhibit shape memory effect and superelasticity. The β -stabilizing elements are further classified into β -isomorphous group and β -eutectoid group. β -isomorphous elements such as V, Zr, Hf, Nb, Ta, Mo and Re stabilize the β phase by forming a simple $\beta \rightarrow \alpha$ transformation while β -eutectoid elements such as Cr, Mn, Fe, Co, Ni, Cu, Pd, Ag, W, Pt and Au stabilize the β phase by forming $\beta \rightarrow \alpha+\gamma$ transformations.

[0050] The stability of the β phase can be expressed as the sum of the weighted averages of the elements that comprise the alloy, often known as the molybdenum equivalent

(Mo_{eq.}). P. Bania, Beta Titanium Alloys in the 1990's, TMS, Warrendale, 1993, defines the Mo_{eq.} in the following equation (1) as

$$\text{Mo}_{\text{eq.}} = 1.00\text{Mo} + 0.28\text{Nb} + 0.22\text{Ta} + 0.67\text{V} + 1.43\text{Co} + 1.60\text{Cr} + 0.77\text{Cu} + 2.90\text{Fe} + 1.54\text{Mn} + 1.11\text{Ni} + 0.44\text{W} - 1.00\text{Al} \quad (1)$$

wherein Mo is molybdenum, Nb is niobium, Ta is tantalum, V is vanadium, Co is cobalt, Cr is chromium, Cu is copper, Fe is iron, Mn is manganese, Ni is nickel, W is tungsten and Al is aluminum and wherein the respective chemical symbols represent the amounts of the respective elements in weight percent based on the total weight of the alloy. In one embodiment, the aluminum can be substituted by carbon, boron, germanium and/or gallium.

[0051] Hf (hafnium), Sn (tin) and Zr (zirconium) exhibit similarly weak effects on the β stability. Although they act to lower the β transus, these elements are considered neutral additions. US Air Force Technical Report AFML-TR-75-41 has suggested that Zr has a small Mo equivalent of 0.25 while Al is an α stabilizer having a reverse effect to that of Mo. Hence, the Mo equivalent in weight percent is calculated according to the following equation (2) which is a modified form of the equation (1):

$$\text{Mo}_{\text{eq.}} = 1.00\text{Mo} + 0.28\text{Nb} + 0.22\text{Ta} + 0.67\text{V} + 1.43\text{Co} + 1.60\text{Cr} + 0.77\text{Cu} + 2.90\text{Fe} + 1.54\text{Mn} + 1.11\text{Ni} + 0.44\text{W} + 0.25(\text{Sn} + \text{Zr} + \text{Hf}) - 1.00\text{Al} \quad (2)$$

[0052] In general it is desirable to have a shape memory alloy that displays superelasticity and/or pseudoelasticity, which has a molybdenum equivalent of about 7 to about 11 wt%, based upon the total weight of the alloy. In one embodiment, it is desirable to have a shape memory alloy that displays superelasticity and/or pseudoelasticity, which has a molybdenum equivalent of about 7.5 to about 10.5 wt%, based upon the total weight of the alloy. In another embodiment, it is desirable to have a shape memory alloy that displays superelasticity and/or pseudoelasticity, which has a molybdenum equivalent of about 8 to about 10 wt%, based upon the total weight of the alloy. In yet another embodiment, it is desirable to have a shape memory alloy that displays superelasticity and/or pseudoelasticity, which has a molybdenum equivalent of about 8.5 to about 9.8 wt%, based upon the total weight of the alloy.

[0053] In one embodiment, the elements present in equation (1) and/or (2) may be optional if desired. In another embodiment, the elements that may be present in the composition in addition to titanium are molybdenum, vanadium, chromium, aluminum, and/or niobium. In yet another embodiment, it is generally desirable for the elements represented in equations (2) to be present in the composition in amounts of greater than or equal to about 0.1, preferably greater than or equal to about 0.5, preferably greater than or equal to about 1, preferably greater than or equal to about 1.5, preferably greater than or equal to about 5, and preferably greater than or equal to about 10 wt%, based upon the total weight of the alloy composition. In yet another embodiment, it is generally desirable for the elements represented in equations (2) to be present in the composition in amounts of less than or equal to about 50, preferably less than or equal to about 40, preferably less than or equal to about 35, preferably less than or equal to about 30, preferably less than or equal to about 25, and preferably less than or equal to about 20 wt%, based upon the total weight of the alloy composition.

[0054] Titanium alloys having a high enough concentration of β stabilizers, generally are sufficiently stable to have a meta-stable β phase structure at room temperature. The alloys showing such a property are called β titanium alloys. Martensite transformations are commonly found among β titanium alloys. The martensitic transformation temperature in β titanium alloys generally decreases with an increasing amount of β stabilizer in the alloy, while increasing the amount of α stabilizer generally raises the martensitic transformation temperature. Therefore, depending on the extent of stabilization, β titanium alloys may exhibit a martensitic transformation when cooled rapidly from temperatures greater than those at which the β phase is the single phase at equilibrium. The β titanium alloy generally comprises an amount of about 8 to about 10 wt% of molybdenum, about 2.8 to about 6 wt% aluminum, up to about 2 wt% chromium, up to about 2 wt% vanadium, up to about 4 wt% niobium, with the balance being titanium. All weight percents are based on the total weight of the alloy. Within the aforementioned range for molybdenum, it is generally desirable to have an amount of greater than or equal to about 8.5, preferably greater than or equal to about 9.0, and more preferably greater than or equal to about 9.2 wt% molybdenum. Also desirable within this range is an amount of less than or equal to about 9.75, and more

preferably less than or equal to about 9.5 wt% molybdenum, based on the total weight of the alloy.

[0055] Within the aforementioned range for aluminum, it is generally desirable to have an amount of greater than or equal to about 2.85, preferably greater than or equal to about 2.9, and more preferably greater than or equal to about 2.93 wt% aluminum. Also desirable within this range is an amount of less than or equal to about 5.0, preferably less than or equal to about 4.5, and more preferably less than or equal to about 4.0 wt% aluminum, based on the total weight of the alloy.

[0056] Within the aforementioned range for vanadium, it is generally desirable to have an amount of greater than or equal to about 1, preferably greater than or equal to about 1.2, and more preferably greater than or equal to about 1.5 wt% vanadium, based on the total weight of the alloy.

[0057] Within the aforementioned range for niobium, it is generally desirable to have an amount of greater than or equal to about 2, preferably greater than or equal to about 3, and more preferably greater than or equal to about 3.5 wt% niobium, based on the total weight of the alloy.

[0058] In one exemplary embodiment, it is generally desirable for the β titanium alloy to comprise 8.9 wt% molybdenum, 3.03 wt% aluminum, 1.95 wt% vanadium, 3.86 wt% niobium, with the balance being titanium.

[0059] In another exemplary embodiment, it is generally desirable for the β titanium alloy to comprise 9.34 wt% molybdenum, 3.01 wt% aluminum, 1.95 wt% vanadium, 3.79 wt% niobium, with the balance being titanium.

[0060] In one embodiment, the β titanium alloy may be solution treated and/or thermally aged. In solution treating the β titanium alloy, the alloy is subjected to a temperature greater than or equal to about 850°C, the β transus temperature for the alloy. The solution treatment of the alloy is normally carried out in either vacuum or inert gas environment at a temperature of about 850 to about 1000°C, preferably about 850 to about

900°C, for about 1 minute or longer in duration depending on the mass of the part. The heating is followed by a rapid cooling at a rate greater than or equal to about 5°C/second, preferably greater than or equal to about 25°C/second, and more preferably greater than or equal to about 50°C/second, by using an inert gas quench or air cooling to retain a fully recrystallized single phase β grain structure. In some instances, it is preferred that the quenched alloy is subsequently subjected to an ageing treatment at about 350 to about 550°C for about 10 seconds to about 30 minutes to adjust the amount of a fine precipitate of the ω phase. In another embodiment, it is desirable to subject the alloy to heat treatment for a time period of up to 8 hours at temperatures of about 350 to about 550°C.

[0061] In another embodiment, the β titanium alloy may be solution treated at a temperature below the β transus temperature of about 750 to about 850°C, preferably about 800 to about 850°C, for about 1 to about 30 minutes to induce a small amount of α precipitates in the recrystallized β matrix. The amount of the α precipitates is preferably less than or equal to about 15 volume percent and more preferably less than or equal to about 10 volume percent, based on the total volume of the composition. This improves the tensile strength to an amount of greater than or equal to about 140,000 pounds per square inch (9,846 kilogram/square centimeter).

[0062] The β titanium alloy in the solution treated condition may exhibit pseudoelasticity. The solution treated β titanium alloy generally exhibits a pseudoelastic recovery of greater than or equal to about 75% of the initial strain when elastically deformed to a 2% initial strain, and greater than or equal to about 50% of the initial strain when elastically deformed to a 4% initial strain. The initial strain is the ratio of the change in length to the original length of the alloy composition.

[0063] The β titanium alloy in the solution treated condition may exhibit linear elasticity. The solution treated β titanium alloy generally exhibits a linear elastic recovery of greater than or equal to about 75% of the initial strain when elastically deformed to a 2% initial strain, and greater than or equal to about 50% of the initial strain when elastically

deformed to a 4% initial strain. The initial strain is the ratio of the change in length to the original length of the alloy composition.

[0064] In another embodiment, the β titanium alloy may be cold worked by processes such as cold rolling, drawing, swaging, pressing, and the like, at ambient temperatures. The β titanium alloy may preferably be cold worked to an amount of about 5 to about 85% as measured by the reduction in cross-sectional area based upon the original cross sectional area. Within this range it is desirable to have a cross sectional area reduction of greater than or equal to about 10, preferably greater than or equal to about 15% of the initial cross sectional area. Also desirable within this range is a reduction in cross sectional area of less than or equal to about 50, more preferably less than or equal to about 30% based on the initial cross-sectional area. The β titanium alloy in the cold worked state (also referred to as the work hardened state) exhibits linear superelasticity where greater than or equal to about 75% of the initial strain is elastically recoverable after deforming to a 2% initial strain, and greater than or equal to about 50% of the initial strain is elastically recoverable after deforming to a 4% initial strain. In one exemplary embodiment related to cold working, the elastic modulus of the β titanium alloy is reduced through cold working by an amount of greater than or equal to about 10, preferably greater than or equal to about 20 and more preferably greater than or equal to about 25% based upon the elastic modulus, after the alloy is heat treated.

[0065] In one exemplary embodiment related to cold working, the elastic modulus of the β titanium alloy is reduced through cold working by an amount of greater than or equal to about 10, preferably greater than or equal to about 20 and more preferably greater than or equal to about 25% based upon the elastic modulus after the alloy is heat treated.

[0066] It is generally desirable to use shape memory alloys having pseudo-elastic properties, and which are formable into complex shapes and geometries without the creation of cracks or fractures. In one embodiment, the β titanium alloy having linear elastic, linearly superelastic, pseudoelastic or superelastic properties may be used in the manufacturing of various articles of commerce. Suitable examples of such articles are eyewear frames, face inserts or heads for golf clubs, medical devices such as orthopedic prostheses, spinal correction devices, fixation devices for fracture management, vascular and non-vascular

stents, minimally invasive surgical instruments, filters, baskets, forceps, graspers, orthodontic appliances such as dental implants, arch wires, drills and files, and a catheter introducer (guide wire).

[0067] In one embodiment, the β titanium alloy having pseudoelastic or superelastic properties may be used in the manufacturing of various articles of commerce. Suitable examples of such articles are eyewear frames, face inserts or heads for golf clubs, medical devices such as orthopedic prostheses, spinal correction devices, fixation devices for fracture management, vascular and non-vascular stents, minimally invasive surgical instruments, filters, baskets, forceps, graspers, orthodontic appliances such as dental implants, arch wires, drills and files, and a catheter introducer (guide wire). Advantages provided by the β titanium alloys are that they are free of nickel, having low modulus, flexible and can be welded, brazed or soldered if desired.

[0068] Figure 1 illustrates a typical eyewear frame 100. Frame 100 includes a pair of rims 110, a bridge 120, a pair of temples 130, and a pair of hinges 140. Rims 110 are joined by bridge 120, which is generally attached to rims 110 by brazing or welding 150. Temples 130 are attached to the hinges 140 by brazing or welding 170, and the hinges 140 are attached to the temples 130. All metal parts of the frame 100 may be formed using β titanium alloys. The β titanium alloys generally provide a lightweight frame with increased spring-back characteristics than conventional titanium alloy frames but with improved adjustability than a superelastic NiTi (nickel titanium) frame. Alternatively, any one or more of the metal parts of the frame 100 may be formed from β titanium alloys. The use of superelastic β titanium alloy is generally preferred in components that require flexibility and adjustability, such as the temples 130. Other components of the frame 100 may be formed using linearly elastic (LE) β titanium alloy, other titanium alloys such as Ti-6Al-4V or commercially pure titanium, other metallic alloys such as stainless steel, CuNi (copper-nickel) alloy or polymeric materials.

[0069] In an alternative embodiment, the temples 130 are formed from a superelastic β titanium alloy, which may be directly connected to the lenses (not shown) of the completed eyewear, thereby eliminating the need for rims 110 and hinges 140. In yet another alternative

embodiment, the superelastic β titanium alloy eyewear may be manufactured by stamping or cutting out the shape of the eyewear frame 100 from a sheet of β titanium alloy, thereby forming a single piece. The piece is then formed into a contour of the frame and heat treated. Grooves are then machined along the edges of the rim 110 to fit lens.

[0070] In yet another embodiment, at least a portion of the frame comprises a linearly superelastic β titanium alloy, while another portion of the frame comprises a linear elastic (LE) β titanium alloys, other titanium alloys such as Ti-6Al-4V or commercially pure titanium, other metallic alloys such as stainless steel, nickel silver alloy or a polymeric resin. When it is desirable to have a portion of the frame comprising a linearly superelastic β titanium alloy, the desired portion is generally cold worked by rolling, drawing, swaging, pressing, or the like.

[0071] Polymeric resins used in the eyewear frames may comprise thermoplastic resins, thermosetting resins, blends of thermoplastic resins with thermosetting resins. In general, the polymeric resin may be derived from a suitable oligomer, polymer, block copolymer, graft copolymer, star block copolymer, dendrimers, ionomers having a number average molecular weight (M_n) of about 1000 grams per mole (g/mole) to about 1,000,000 g/mole. Suitable examples of thermoplastic resins include polyacetal, polyacrylic, styrene acrylonitrile, acrylonitrile-butadiene-styrene, polycarbonates, polystyrenes, polyethylene, polypropylenes, polyethylene terephthalate, polybutylene terephthalate, polyamides such as nylon 6, nylon 6,6, nylon 6,10, nylon 6,12, nylon 11 or nylon 12, polyamideimides, polybenzimidazoles, polybenzoxazoles, polybenzothiazoles, polyoxadiazoles, polythiazoles, polyquinoxalines, polyimidazopyrrolones, polyarylates, polyurethanes, thermoplastic olefins such as ethylene propylene diene monomer, ethylene propylene rubber, polyarylsulfone, polyethersulfone, polyphenylene sulfide, polyvinyl chloride, polysulfone, polyetherimide, polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy polymer, polychlorotrifluoroethylene, polyvinylidene fluoride, polyvinyl fluoride, polyetherketone, polyether etherketone, polyether ketone ketone, or the like, or combinations comprising at least one of the foregoing thermoplastic resins.

[0072] Suitable examples of blends of thermoplastic resins include acrylonitrile-butadiene-styrene/nylon, polycarbonate/acrylonitrile-butadiene-styrene, acrylonitrile-butadiene-styrene/polyvinyl chloride, polyphenylene ether/polystyrene, polyphenylene ether/nylon, polysulfone/acrylonitrile-butadiene-styrene, polycarbonate/thermoplastic urethane, polycarbonate/polyethylene terephthalate, polycarbonate/polybutylene terephthalate, thermoplastic elastomer alloys, nylon/elastomers, polyester/elastomers, polyethylene terephthalate/polybutylene terephthalate, acetal/elastomer, styrene-maleicanhydride/acrylonitrile-butadiene-styrene, polyether etherketone/polyethersulfone, polyethylene/nylon, polyethylene/polyacetal, or the like, or combinations comprising at least one of the foregoing thermoplastic blends.

[0073] Suitable examples of polymeric thermosetting materials include polyurethanes, natural rubber, synthetic rubber, epoxy, phenolic, polyesters, polyamides, silicones, or the like, or combinations comprising at least one of the foregoing.

[0074] For the frame 100, it is generally desirable to have the temples 130 manufactured from superelastic or linearly superelastic β titanium alloy. While many variations of temple 130 are available in the eyewear manufacturing industry, the temple 130 is shown in Figure 2 one possible construction. The temple 130 includes a tapered end 210, a pressed end 220, a hinge 140, a rim connector 240, and a hinge cut 250.

[0075] In temple 130, the tapered end 210 and the pressed end 220 are formed from a continuous piece of β titanium alloy wire. The hinge 140 and the rim connector 240 are each joined to the pressed end 220, typically by brazing. Hinge cut 250 generally permits a free rotation of the hinge 140. The hinge 140 and the rim connector 240 may also be fabricated from β titanium alloys or from other suitable material such as titanium or nickel silver alloys, if desired.

[0076] The superelastic β titanium alloy generally provides an adequate spring-back for eyewear applications. It is generally desired to use superelastic β titanium alloy having a minimum recovery of about 50%, based on the outer fiber bend strain, when the alloy is deformed to an outer fiber strain of about 4%. Within this range, it is more preferably greater than or equal to about 75%, when the alloy is deformed to about 4% outer fiber strain.

[0077] It is also generally desirable for the superelastic β titanium alloy to have a minimum recoverable strain of about 2%, based on the original length when the alloy is deformed to about 4% in tensile strain. Within this range, it is generally desired to have a minimum recovery of greater than or equal to about 3% when the alloy is deformed to about 4% tensile strain in the tensile test.

[0078] The eyewear frame may be manufactured by a variety of different methods used to shape or form metals and alloys. In one embodiment, the desired shape of the eyewear frame 100 is stamped from a sheet of β titanium alloy, thereby forming a single piece. In another embodiment, the basic shape may be formed of wires using mechanical shaping methods.

[0079] For example, in the manufacture of temple 130, a β titanium alloy wire is modified to provide the basic shape of temple 130. The superelastic β titanium alloy wire is first swaged, creating multiple sections having consecutively decreasing diameters, and then a number of the largest sections are pressed to flatten them. The eyewear frame 100 can also be fabricated from wires via cold forming and shape-setting heat treatment processes. The eyewear frame 100 can also be fabricated from superelastic β titanium alloys sheets or wires by laser cutting, chemical etching or other cutting means followed by shape-setting heat treatment or other forming and heat treating processes.

[0080] The eyewear frame 100 may optionally be annealed to regain workability and to overcome brittleness induced by cold working. Cold working of β titanium alloys (e.g., swaging, pressing) generally alter its mechanical properties, causing it to become stronger and more brittle. Annealing at temperatures of greater than or equal to about 850°C for about 1 to about 30 minutes may be used to soften the material, rendering it more ductile and formable.

[0081] Following the manufacturing of the eyewear frame 100 and the optional annealing, it may be desired to attach additional components to the frame. For example, in a general eyewear manufacturing process, the hinge 140 and the rim connector 240 are brazed or soldered to the temple 130, and the temple 130 may be cut to permit the hinge 140 to rotate.

[0082] Where desired, the eyewear frame 100 may be subjected to a polishing operation in order to give the frame a smooth appearance and to remove any rough edges. For example, the eyewear frame 100 can be polished by high energy barrel tumbling and then plated by processes such as chemical vapor deposition, electroplating, and the like, to prepare the frame for additional finishing steps. This plating is preferably accomplished using gold or nickel.

[0083] After the plating operation, the eyewear frame 100 may be optionally heat-treated at a temperature of about 350 to about 450°C for a period of about 10 minutes in order to infuse the gold or nickel layer deposited on the frame into the β titanium alloy. The eyewear frame is then be subjected to additional finishing processes to provide a desirable aesthetic appearance. For example, the frame may be plated with a metal, such as gold, chrome, or platinum. A protective coating, such as a light spray of epoxy, may be added to seal and protect the frame. If desired, the frame is subjected to adjustments by the user to further shape the eyewear frame 100.

[0084] In another embodiment, the β titanium alloy may be used to manufacture at least a portion of a golf club. The β titanium alloy may be also be used to manufacture a golf club head. In an exemplary embodiment, the β titanium alloy may be used to manufacture face inserts, which are mounted into the golf club head.

[0085] Figure 3A shows an insert 2 that substantially follows the contours of the golf club head. The bevel is designed such that when the insert is mounted into the golf club head mating cutout or pocket, the insert will be retained securely in the club head even during the violent swings encountered while playing golf. The bevel is generally at an angle of about 30 to about 60 degrees with respect to a perpendicular to the back 8 of the insert and extends around the bottom and the two sides adjacent to the bottom edge of the insert 2 as shown in Figure 3A. The insert 2 generally has a thickness of about 0.010 (0.0254 centimeter) to about 0.93 inches (2.36 centimeters). In an exemplary embodiment, the insert may have a variable thickness across its cross section if desired.

[0086] Figure 3B shows another embodiment of the insert. Here a tongue 9 is formed on opposing sides of the insert to secure the insert in a corresponding groove in the golf club

head. Figure 4A shows a pocket 12 formed in the face of a club head 14 into which an insert 2 having beveled edges may be disposed. The pocket is formed from the bottom of the club head and extends upward. However, the pocket does not extend to the top edge of the club head, there remains a narrow channel 16 between the top of the pocket and the top of the golf club head. The insert is preferably wedge shaped and the angle is preferably about 2 degrees.

[0087] Referring to Figure 4B the pocket in the golf club head has a grooved edge 18 that extends around the three sides (left, right and top) of the pocket. The groove 18 is arranged to be in mechanical communication with the tongue 9 of an insert. The insert may be secured within the club head by cement, polymeric resins such as epoxy, acrylates, methacrylates, silicones, or the like. Figure 5 shows another golf club head 20 with an insert 22 that extends from the top to the bottom of the golf club head 20. In this instance, the bottom and top edges of the insert are flush with the bottom and top edge of the golf club head 20. Grooved edges 24 may be used to retain the insert 2 in the golf club head 20.

[0088] Figure 6A provides a front view of a golf club face 40 with the insert 42. The insert 42 covers the striking area of the golf club head and the golf club head 44 forms a margin around the insert. Figure 6B shows one configuration of the cross sectional view of the golf club head 44 as a casting. Forged and machined golf club heads 44 may also be used. The golf club head 44 has a cavity 46 into which the insert 42 is placed. Ears 48 extend out from the golf club head 44 as shown and the inserts have grooves 50 designed to receive the ears. The ears are swaged over into the grooves as shown in Figure 6C. The rough edges may then be finished to form a golf club head 44 having a smooth club face as shown in Figure 6D.

[0089] In one embodiment related to the assembly of the insert into the golf club head in Figures 3A, 3B, 4A, 4B, 5, 6A – D, the insert may be held in place in a slot in the golf club head through friction or other mechanical means. When friction is employed, the insert is held in position in the golf club head via a tight toleranced fit. In an exemplary embodiment, the insert is assembled in the golf club head via brazing or welding. This facilitates ease of manufacture and assembly of the golf club head when compared with other methods of manufacturing.

[0090] In another embodiment, the β titanium alloy may be used in a catheter having an implantable stent as shown in Figure 26. In the Figure 26, the distal end of a catheter 115 having a stent 165 carried within it for implantation into the body of a patient. The proximal end of the catheter 115 is connected to a suitable delivery mechanisms and the catheter 115 is of sufficient length to reach the point of implantation of the stent 165 from the introduction point into the body. As used herein, the term "proximal" refers to a location on the catheter closest to the clinician using the device and thus furthest from the patient on which the device is used. Conversely, the term "distal" refers to a location farthest from the clinician and closest to the patient.

[0091] The catheter 115 includes an outer sheath 105, a middle tube 125 which may be formed of a compressed spring, and a flexible (e.g., polyamide) inner tube 145. A stent 165 for implantation into a patient is carried within the outer sheath 105. The stent 165 is generally manufactured from a shape memory alloy frame 185, which is formed in a criss-cross pattern, which may be laser cut. One or both ends of the stent 165 may be left uncovered as illustrated at 225 and 245 to provide anchoring within the vessel where the stent 165 is to be implanted.

[0092] A radiopaque atraumatic tip 265 is generally secured to the end of the inner tube 145 of the catheter. The atraumatic tip 265 has a rounded end and is gradually sloped to aid in the movement of the catheter through the body vessel. The atraumatic tip 265 is radiopaque so that its location may be monitored by appropriate equipment during the surgical procedure. The inner tube 145 is hollow so as to accommodate a guide wire, which is commonly placed in the vessel prior to insertion of the catheter, although a solid inner section and be used without a guide wire. Inner tube 145 has sufficient kink resistance to engage the vascular anatomy without binding during placement and withdrawal of the delivery system. In addition, inner tube 145 is of sufficient size and strength to allow saline injections without rupture.

[0093] A generally cup-shaped element 285 is provided within the catheter 115 adjacent the rear end of the stent 165 and is attached to the end of the spring 125 by appropriate means, e.g., the cup element 285 may be plastic wherein the spring 125 is molded

into its base, or the cup element 285 may be stainless steel wherein the spring 125 is secured by welding or the like. The open end of the cup element 285 serves to compress the end 245 of the stent 165 in order to provide a secure interface between the stent 165 and the spring 125. Alternatively, instead of a cup shape, the element 285 could be formed of a simple disk having either a flat or slightly concave surface for contacting the end 245 of the stent 165.

[0094] In yet another embodiment, the β titanium alloy may be utilized as an intravenous (IV) catheter to introduce certain fluids such as saline solution directly into the bloodstream of a patient. Typically, a needle or other stylet made from the β titanium alloy is first introduced through the cannula portion of the catheter and into the skin of the patient at the desired location such as the back of the patient's hand or a vessel on the inside of the arm. Once insertion is complete, the needle is removed from the cannula portion of the catheter. After removing the needle, a fluid handling device such as a syringe is attached to the luer fitting located at the proximal end of the catheter hub. Fluid then flows directly from the fluid handling device through the catheter into the bloodstream of the patient. When the needle is removed from the cannula, the health care worker must place the exposed needle tip at a nearby location while simultaneously addressing the task required to accomplish the needle removal. It is at this juncture that the exposed needle tip creates a danger of an accidental needle stick occurring which leaves the health care worker vulnerable to the transmission of various, dangerous blood-borne pathogens such as human immune virus (HIV) and hepatitis.

[0095] As used herein, the term "proximal" refers to a location on the catheter and needle assembly with needle tip protector closest to the clinician using the device and thus furthest from the patient on which the device is used. Conversely, the term "distal" refers to a location farthest from the clinician and closest to the patient.

[0096] As illustrated in Figures 27 and 28, the IV catheter assembly 201 comprises catheter assembly 221 and needle assembly 241. Needle assembly 241 further includes protector 261. Catheter assembly 221 includes catheter 281, which is a tubular structure having a proximal end 311 and distal end 291. Proximal end 311 of catheter 281 is fixedly attached to catheter hub 301. Catheters are well known in the medical art and one of many

suitable materials, most of which are flexible thermoplastics, may be selected for use in catheter 281. Such materials may include, for example, polyurethane or fluorinated ethylene propylene. Catheter hub 301 is a generally tubular structure having an internal cavity in fluid communication with the internal lumen of catheter 281. Catheter hub 301 may be made from a suitable, rigid medical grade thermoplastic such as, for example, polypropylene or polycarbonate. For illustration purposes catheter hub 301 is shown translucent, though in actual use it may be translucent or opaque. At the proximal end of catheter hub 301 is integrally attached Luer fitting 321. Luer fitting 321 provides for secure, leak proof attachment of tubing, syringes, or any of many other medical devices used to infuse or withdraw fluids through catheter assembly 221. As shown in Figures 27 and 28, retainer 601, which is located approximately mid way between the proximal end and distal end of sidewall 361 and fixedly attached thereto, includes aperture 621 which is an opening therethrough. Retainer 601 is generally a doughnut shaped washer made of a material such as, for example, silicone or polytetrafluoroethylene. The retainer 601 generally secures the protector 261 in catheter hub 301.

[0097] Referring again to Figures 27 and 28, needle assembly 241 comprises needle 381, which is a tubular structure with proximal end 391 and distal end 411, needle hub 401, and protector 261. Protector 261 is assembled slidably on needle 381. Needle 381, which is preferably made of stainless steel has a lumen therethrough created by its inner diameter. Proximal end 391 of needle 381 is fixedly attached to needle hub 401. Bevel 421, which is located at distal end 411 of needle 381 creates a sharp piercing tip. Needle groove 441, which includes proximal wall 431 and distal wall 451, is located at distal end 411 of needle 381 proximal to bevel 421 and is smaller in diameter than the nominal outer diameter of needle 381. Needle groove 441 may be created by machine grinding around the outside diameter of needle 381 resulting in an annular channel between its nominal outer diameter and inner diameter. The resulting groove 441 is smaller in dimension than the nominal outer diameter of needle 381 but greater in dimension than the lumen in needle 381 and generally prevents the complete removal of protector 261 from needle 381. In the preferred embodiment, the dimension across groove 441 is about 0.002 to about 0.003 inches (about

0.0508 to about 0.0762 millimeter) smaller than the dimension of the nominal outer diameter of needle 381, dependent upon needle "gauge" size.

[0098] Needle hub 401 is generally a tubular structure having an internal cavity in fluid communication with the lumen in needle 381. It is preferably made of a translucent or transparent generally rigid thermoplastic material such as, for example, polycarbonate. At the most proximal end of the internal cavity in needle hub 401 is fixedly attached a porous plug 461. A flashback chamber 481 is created in the cavity distal to porous plug 461. Porous plug 461 contains a plurality of microscopic openings, which are large enough to permit the passage of air and other gasses but small enough to prevent the passage of blood. Flashback chamber 481 fills with blood upon successful entry of the needle tip into the targeted vein, providing the clinician visual conformation of the correct placement of the needle.

[0099] In one embodiment, the β titanium alloy may be used as an orthopedic device such as a fixation device for bones in the hip, knee, spine, or the like. A suitable example of one configuration of a bone fixation device shown in Figures 29, 30 and 31 is a threaded bone screw. Figures 29, 30 and 31 show a cannulated, internally and externally threaded bone screw 202 and a cannulated driver device 222 constructed from a β titanium alloy. The driver device 222 includes a shaft member 262 defining a throughgoing bore 272, a handle 282 and includes a rod 302 and a cap member 322. The rod 302 and cap member 322 are used to releasably secure the bone screw 202 to the driver device 222 as will later be described. The shaft member 262 is an elongated, generally cylindrical structure, which has a cylindrical throughgoing bore or cannula 272 best seen in the cross-sectional view of Figure 31 which extends longitudinally from a proximal end 342 of the shaft member 262 to a distal end 362.

[0100] The shaft member 262 is an integral tubular structure preferably constructed of surgical steel, although any suitable material such as β titanium alloy can be used, and includes a shaped engagement structure 382 integrally formed at the distal end 362 and one or more annular grooves 372 spaced along its length. The engagement structure 382, which preferably has a hexagonal configuration facilitates the mating and rotational engagement of the bone screw 202 with the driver as will be described and the grooves 372 may be used as attachment sites for conventional clamp members during a bone fixation procedure. It will be

appreciated that the engagement structure 382 may take any angular configuration such as square, octagonal or the like and can alternatively engage the outer periphery of the screw head.

[0101] The handle 282 has a throughgoing bore 392 to receive the proximal end 342 of the shaft member 262 and is preferably constructed of wood or plastic. The handle 282 is secured to the shaft member 262 by securing the handle sections together with conventional rivets 392 or by other suitable means. The rivets do not extend into or through the bore of the shaft member 262. Alternatively, the handle member 282 may be removably mounted to the shaft member 262.

[0102] The rod 302 is an integral, solid, generally cylindrical structure preferably constructed of surgical or high grade steel and is provided with a threaded section 422 at its distal end and a machined recess or well 44 near its proximal end which receives set screw 472. The cap member 322 is a generally cylindrical structure that has a blind bore 432 to receive the proximal end of the rod 302 and a cylindrical, internally threaded passage 452 which extends from a side surface of the cap member 322 into the blind bore 432 to permit the passage of a conventional set screw 472 having an Allen head. A conical end portion of the Allen set screw is received within the well 44 in the rod 302 to lock the cap member 322 to the rod 302. The outer surface of cap 322 is knurled at 332 to allow the cap 322 and secured rod 302 to be rotated within bore 272 of the shaft 262 so that threaded end 422 can be screwed into the inner thread 582 of the cannulated bone screw 202.

[0103] The outer diameter of the cylindrical rod 302 is less than the inner diameter of the cylindrical bore 272 in the shaft member 262 so that the rod 302 can be easily received therein and pass therethrough. Conversely the threaded end section 422 has threads with an outer diameter greater than the outer diameter of bore 272 so that rod 302 cannot be pulled through the bore 272 of the shaft 262. When the cap member 322 is releaseably locked to the proximal end of the rod 302, cap member 322 prevents a portion of the proximal end of the rod 302 from entering the cannula 272 of the shaft member 262. As best seen in Figure 31, the rod 302 is longer than the shaft member 262 so that when the cap member 322 is mounted on the rod 302 and the rod 302 is disposed within the cannula or bore 272 of the shaft

member 262, the threaded section 422 of the rod 302 extends a predetermined length beyond the distal end 362 of the shaft member 262 to threadedly engage the internal threading 582 of the bone screw 202. The orthodontic device may be advantageously used in other body tissue in all living beings. Other examples of orthodontic devices are those, which may be used in hip, knee, shoulder implants, intermedullary rods and nails, fracture fixation devices, spinal fusion and correction instruments.

[0104] In another embodiment, the β titanium alloy may be used in orthodontic devices such as orthodontic arch wires. One possible configuration of an orthodontic arch wire 103 is shown in Figures 32 and 33, and includes an anterior segment 113, and a pair of posterior segments 123 and 133 secured to and extending from the respective ends of the anterior segment. The anterior segment may be made of a material having a stiffness or flexural rigidity, which is less than that of the material forming the posterior segments. The segments can be secured together by using any of several different attachment techniques. In the form shown in Figures 32 and 33, a crimpable metal tube 153 is provided at each segment junction for mechanical attachment of the segments. As shown in Figure 32, the β titanium alloy arch wire 103 is of conventional generally U-shaped configuration for conformation with the patient's dental arch. The arch is equally useful with lingual brackets and related appliances, which are mounted on the rear surfaces of the teeth. Figure 34 shows a so-called "mushroom" arch wire 203, which is again of generally U-shaped configuration, but is contoured to conform to the curvature of the lingual or inner surfaces of the teeth. Arch wire 203 includes an anterior segment 213 of relatively low stiffness, a pair of posterior segments 223 and 233 of relatively higher stiffness, and crimped tubes 243 joining the segments and positioned to be just distal of the cuspids when installed. Other dental applications include arch wires, dental implants, files and drills used in orthodontic work.

[0105] The β titanium alloy has a number of advantages. The elastic modulus of the β titanium alloy is advantageously reduced through cold working by an amount of greater than or equal to about 10, preferably greater than or equal to about 20 and more preferably greater than or equal to about 25% based upon the elastic modulus after the alloy is heat treated. The β titanium alloy may preferably be cold worked to an amount of about 5 to about 85% as measured by the reduction in cross-sectional area based upon the original cross sectional area.

Within this range it is desirable to have a cross sectional area reduction of greater than or equal to about 10, preferably greater than or equal to about 15% of the initial cross sectional area. Also desirable within this range is a reduction in cross sectional area of less than or equal to about 50, more preferably less than or equal to about 30% based on the initial cross-sectional area. When cold worked, the β titanium alloy may have a pseudoelastic strain recovery of greater than or equal to about 75% of the applied strain, when the applied strain is up to about 2% of the original length and of greater than or equal to about 50% of the applied strain, when the applied strain is up to about 4% of the original length. (i.e., the change in length is 4% of the original length).

[0106] The following examples, which are meant to be exemplary, not limiting, illustrate the methods of manufacturing for some of the various embodiments of the articles prepared from the β titanium alloys described herein.

EXAMPLES

EXAMPLE 1

[0107] All of the sample alloys discussed below were prepared by a double vacuum arc melting technique. The ingots were hot rolled and flattened to sheets having a thickness of 1.5 millimeter (mm). The sheets were then heat treated at 870°C for 30 minutes in air and air cooled to ambient temperature. Oxides on the sheets were removed by double-disc grinding and lapping to a thickness of 1.3 mm. Heat aging experiments were conducted at 350°C using a nitride/nitrate salt bath.

[0108] Permanent deformation and pseudo-elastic recovery strains were determined using bend tests. Specimens having dimensions 0.51 mm x 1.27 mm x 51 mm were cut from the sheets. The specimens were bent against a rod of approximately 12.2 mm in diameter to form a "U" shape to yield an outer fiber or outer surface strain close to 4%. The angles

between the straight portions were measured afterwards and the strain recovery calculated by using the formula:

$$e(\text{rec}) - e(180-a)/180;$$

where "a" is the unrecovered angle and "e" is the outer-fiber bending strain.

[0109] Tensile strain recovery was measured by tensile elongation to a strain of 4% followed by unloading to zero stress. Tensile specimens with a cross sectional dimension of 0.90 mm x 2.0 mm were used and the strain was monitored using an extensometer. An environmental chamber with electrical heating and CO₂ cooling capabilities provided a testing capability from -30°C to 180°C.

[0110] Nine β titanium alloys having the compositions listed in Table 1 were examined. The percentage of the elastic recovery strain with respect to the total bend strain was measured for comparison.

Table 1

| Sample # | Titanium | Molybdenum | Niobium | Vanadium | Aluminum |
|----------|----------|------------|---------|----------|----------|
| 1 | Balance | 7.63 | 3.98 | 2.05 | 3.10 |
| 2 | Balance | 8.03 | 3.89 | 2.03 | 3.09 |
| 3 | Balance | 8.40 | 3.83 | 1.94 | 3.03 |
| 4 | Balance | 8.97 | 3.86 | 1.95 | 3.03 |
| 5 | Balance | 9.34 | 3.79 | 1.95 | 3.01 |
| 6 | Balance | 10.35 | 3.83 | 1.99 | 3.02 |
| 7 | Balance | 10.83 | 3.88 | 2.01 | 3.02 |
| 8 | Balance | 11.48 | 4.00 | 2.04 | 3.15 |
| 9 | Balance | 11.68 | 3.89 | 1.98 | 3.07 |

[0111] In the Table 1 above Sample 1 and Samples 6 – 9 are comparative examples. The results of elastic recovery after bending to approximately 4% outer fiber strain is graphically demonstrated in Figure 7. The figure shows a maximum elastic strain recovery at about 9 wt% molybdenum, where the alloy after solution heat treatment and subsequent air cooling, exhibits an elastic recovery strain of approximately 80% of the applied 4% deformation strain. Increasing or decreasing the molybdenum content from 9 wt% generally results in decreasing elastic recovery. It may also be seen that an aging treatment at 350°C for a short duration of 10 seconds results in an improved elastic recovery, for titanium alloys having a molybdenum content between 8.4 and 11 wt%. The optimal elastic strain recovery after heat aging at 350°C for 10 seconds for the alloy having about 9 wt% molybdenum is approximately 90% of the applied 4% bend strain. Alloys with a molybdenum content less than 8.4 wt% exhibit a different aging characteristic. Aging at 350°C may degrade elastic strain recovery as for alloy 2 having about 8.03 wt% molybdenum, or has no significant effect as for alloy 1 having about 7.63 wt% molybdenum.

[0112] The percent of the elastic recovery to the total deformation during thermal aging at 350°C for Samples 4, 5 and 6 respectively, are plotted in the Figures 8, 9 and 10 respectively. From the Figures 8, 9 and 10 it may be seen that the elastic recoveries of all three alloys reach a maximum after aging for about 10 to about 60 seconds. Aging beyond 15 minutes (900 seconds) degrades the elastic recovery.

[0113] The percents of the elastic recovery to the total deformation during thermal aging at about 250 to about 550°C for 10 seconds for Samples 4 and 5 respectively are plotted in the Figures 11 and 12, respectively. An optimal for Sample 4 appears at 350°C, which improves the elastic recovery to a percentage close to 90% while aging at temperatures equal to or higher than 400°C degrades elastic recovery to about 40%. For Sample 5, aging in this temperature range generally improves the elastic recovery. The maximum improvement occurs at about 450°C where the elastic recovery is improved to 90%.

[0114] The alloys shown in Table I also exhibit linear superelasticity after cold working with a reduction of greater than or equal to about 30% in the cross-sectional area.

For example, a wire fabricated from an ingot having a composition of 11.06 wt% molybdenum, 3.80 wt% niobium, 1.97 wt% vanadium, 3.07 wt% aluminum with the remainder being titanium exhibited an elastic recovery strain of 3.5% after bending to a total deformation of 4% outer fiber strain, when the reduction in the cross sectional area after cold working was 84%.

EXAMPLE 2

[0115] In this example, the β titanium alloys were manufactured by double vacuum arc melting. Chemistries of the alloys were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OE). The results are tabulated in Table 2. The ingot was hot-forged, hot-rolled and finally cold-drawn to wire of various diameters in the range of about 0.4 to about 5 mm. Inter-pass annealing between cold reductions was carried out at 870°C in a vacuum furnace for wires having a diameter of larger than 2.5 mm or by strand annealing under inert atmosphere for the smaller diameters. Tensile properties were determined using an Instron model 5565 material testing machine equipped with an extensometer of 12.5 mm gage length. Microstructures were studied by optical metallography using a Nikon Epiphot inverted metallurgical microscope.

Table 2

| Sample # | Titanium | Molybdenum | Niobium | Vanadium | Aluminum | MoEq |
|----------|----------|------------|---------|----------|----------|-------|
| 10 | Balance | 11.06 | 3.80 | 1.97 | 3.07 | 10.37 |
| 11 | Balance | 9.59 | 3.98 | 1.99 | 3.13 | 8.91 |

[0116] The strand-annealed wires generally have a higher ultimate tensile strength (UTS) around 1055 mega Pascals (MPa) than vacuum annealed wires and sheets, the typical UTS of which is about 830 MPa. Figure 13 plots the UTS of wires drawn from an annealed 1.0 mm diameter Sample 11 wire stock as a function of reduction in cross-section area. After a 49% reduction, the UTS was elevated from 1055 MPa to only 1172 MPa indicating a fairly weak strain hardening effect. Young's Modulus was determined by tensile testing the wire to 1% strain and measuring the linear slope of the stress-strain curve. As shown in Figure 14, cold-drawn wires generally have a lower modulus than does annealed wire. The modulus, of approximately 65.9 gigapascals (GPa) for the annealed wire, decreases with increasing accumulative amount of reduction and stabilizes at approximately 50 GPa after cold drawing with a cumulative reduction greater than 20%.

[0117] Similar to alloys in Table 1, Samples 10 and 11 exhibit linear superelasticity after cold working. Loading and unloading stress-strain curves tested to 2% and 4% tensile

strains of a cold drawn, 0.91 mm diameter wire of Sample 11 with a 19.4% reduction are plotted in Figures 15 and 16, respectively. As may be seen in Figure 13, after unloading, following a 2% tensile elongation, the wire recovers the majority of the deformation leaving only a small plastic deformation of 0.1% strain. When deformed to a 4% tensile elongation, the residual strain after unloading increases to 1.4%. The wire recovers a strain of 2.6%. The residual strain decreases with increasing drawing (cross-sectional area) reduction. However, when the reduction exceeds 20%, specimens failed before reaching a 4% tensile elongation. As this data suggests, cold drawn β titanium alloy wires exhibit linear superelasticity and are capable of recovering large deformations greater than the typical elastic limit for conventional metallic alloys. The mechanical property of cold-drawn wire appears to be insensitive to chemical composition as the cold-drawn Sample 10 exhibits similar mechanical properties. All the loading/unloading tensile test results for Sample 10 are tabulated in Tables 3.

Table 3.

| Cold Work Amount (%) | 21 | 37 | 50 | 61 | 69 |
|-----------------------------|-----|-----|-----|-----|-----|
| Tested to 2% tensile strain | | | | | |
| Elastic Strain (%) | 1.9 | 1.8 | 1.8 | 1.9 | 2.0 |
| Plastic Strain (%) | 0.1 | 0.2 | 0.2 | 0.1 | 0.0 |
| Tested to 3% tensile strain | | | | | |
| Elastic Strain (%) | 2.5 | 2.6 | 2.6 | 2.7 | 2.7 |
| Plastic Strain (%) | 0.5 | 0.4 | 0.4 | 0.3 | 0.3 |
| Tested to 4% tensile strain | | | | | |
| Elastic Strain (%) | --- | 2.8 | 2.9 | 3.1 | 3.2 |
| Plastic Strain (%) | --- | 1.2 | 1.1 | 0.9 | 0.8 |

[0118] A micrograph in Figure 17 reveals the cold-worked microstructure of the Sample 10 wire after a 14% cold working reduction in cross sectional area. The recrystallized microstructures of the wire after heat-treatments at 816°C and 871°C for 30 minutes are shown in Figures 18 and 19, respectively. It is apparent that the material was not fully betatized after the heat-treatment at 816°C as α phase was present in the microstructure.

As may be seen in Figure 17, a fully recrystallized β grain structure was obtained after the heat-treatment at 871°C for 30 minutes.

[0119] Sample 10 wires hot-rolled to 8.6 mm in diameter were further drawn down to 6.0 mm diameter. After being fully betatized at 871°C for 30 minutes the 6.0 mm diameter wires were again aged at temperatures of about 500 to about 850°C for 30 minutes. As can be seen in Figure 20, the β structure was preserved after aging at 816°C. When the aging temperature was lowered to 788°C, intragranular α -phase precipitates began to appear in the microstructure as may be seen in Figure 21. The amount of intragranular α -phase precipitate increased with decreasing aging temperature. α -phase precipitates eventually appeared along the grain boundary when aged at 649°C and below.

[0120] The ultimate tensile strength (UTS) and tensile ductility (% reduction in cross-section area) of betatized Sample 10 from Table 2 after aging at a temperature of about 500 to about 900°C for 30 minutes are plotted in Figures 22 and 23, respectively. Fully betatized specimens such as solution-treated specimens and those aged at 816°C and above, exhibited a low UTS of about 800 MPa and a good tensile ductility of about 25 to about 30% in reduction in cross-section area (RA). As the aging temperature decreased, there was a drastic increase in UTS with a significant reduction in tensile ductility, presumably due to an increasing amount of α -precipitates. The peak of 1400 MPa in UTS coincides with the low in ductility (5% RA) and both appeared at approximately 500°C of aging temperature.

[0121] The Sample 11 composition in solution treated condition exhibits pseudoelasticity. Their mechanical properties are highly sensitive to solution heat treatment and subsequent aging at a temperature of about 350 to about 550°C. It was discovered that Sample 11 wires after strand annealing at 870°C exhibit well-defined pseudoelasticity. An example is presented in Figure 24, which shows a 4% tensile stress-strain curve of a strand-annealed, 0.4mm diameter Sample 11 wire. After deforming to a 4% elongation, the wire specimen was able to go through a pseudoelastic recovery recovering a 3.4% tensile strain and leaving a residual strain of only 0.6% after unloading.

[0122] A transverse cross-sectional view of the wire microstructure is shown in a

micrograph of Figure 25. Instead of the anticipated β structure, the microstructure consists of equiaxial α precipitates in β matrix. It appears that the short duration of strand annealing did not allow the wire to fully recrystallize into the β grain structure. Without being limited by theory, it is believed that this may explain why strand-annealed wire generally has a higher UTS when compared to that of a fully betatized material.

[0123] As may be seen from the above experiments, the β titanium alloys can display an elastic strain recovery of 88.5%, when subjected to an initial bending strain of 4%. The strain recovery is measured as a function of the initial bending strain and the initial bending strain is expressed as a percentage of the ratio of the change in length to the original length. These alloys may be advantageously used in a number of commercial applications such as eyewear frames, face insert and heads for golf clubs, orthodontic arch wires, orthopedic prostheses and fracture fixation devices, spinal fusion and scoliosis correction instruments, stents, guide wires, stents, filters, graspers, baskets, eyewear, golf club, a catheter introducer (guide wire) and the like.

[0124] While the invention has been described with reference to exemplary embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention.

What is claimed is:

1. An article manufactured from a composition comprising:

titanium; and

a molybdenum equivalent weight of about 7 to about 11 wt%, wherein the weight percents are based upon the total weight of the alloy composition, wherein the composition is superelastic and/or pseudoelastic.

2. The article of Claim 1, wherein the molybdenum equivalent weight is determined by the equation (1)

$$\text{Mo}_{\text{eq.}} = 1.00\text{Mo} + 0.28\text{Nb} + 0.22\text{Ta} + 0.67\text{V} + 1.43\text{Co} + 1.60\text{Cr} + 0.77\text{Cu} + 2.90\text{Fe} + 1.54\text{Mn} + 1.11\text{Ni} + 0.44\text{W} - 1.00\text{Al} \quad (1)$$

or the equation (2)

$$\text{Mo}_{\text{eq.}} = 1.00\text{Mo} + 0.28\text{Nb} + 0.22\text{Ta} + 0.67\text{V} + 1.43\text{Co} + 1.60\text{Cr} + 0.77\text{Cu} + 2.90\text{Fe} + 1.54\text{Mn} + 1.11\text{Ni} + 0.44\text{W} + 0.25(\text{Sn} + \text{Zr} + \text{Hf}) - 1.00\text{Al} \quad (2)$$

wherein Mo is molybdenum, Nb is niobium, Ta is tantalum, V is vanadium, Co is cobalt, Cr is chromium, Cu is copper, Fe is iron, Mn is manganese, Ni is nickel, W is tungsten, Al is aluminum, S is tin, Zr is zirconium and Hf is hafnium; wherein the aluminum can be substituted by carbon, boron, germanium and/or gallium; and wherein the respective chemical symbols represent the amounts of the respective elements in weight percent based on the total weight of the alloy composition.

3. The article of Claim 1, having a composition comprising:

about 8 to about 10 wt% molybdenum,

about 2.8 to about 6 wt% aluminum,

up to about 2 wt% chromium,

up to about 2 wt% vanadium,

up to about 4 wt% niobium, with the balance being titanium, wherein the weight percents are based on the total weight of the alloy composition.

4. The article of Claim 1, wherein the composition is cold worked and/or solution treated.

5. The article of Claim 1, wherein the composition has an elastic recovery of greater than or equal to about 75% of the applied change in length, when the applied change in length is 2% of the original length.

6. The article of Claim 1, wherein the composition has an elastic recovery of greater than or equal to about 50% of the applied change in length when the applied change in length is 4% of the original length. .

7. The article of Claim 1, wherein the composition after cold working has a reduction in the elastic modulus of greater than or equal to about 10% when compared with the elastic modulus of an equivalent heat treated composition.

8. The article of Claim 1, wherein the composition after cold working has a reduction in the elastic modulus of greater than or equal to about 20% when compared with the elastic modulus of an equivalent heat treated composition.

9. The article of Claim 1, wherein the composition after cold working has a reduction in the elastic modulus of greater than or equal to about 25% when compared with the elastic modulus of an equivalent heat treated composition.

10. The article of Claim 1, wherein the composition has a β phase or an α phase and a β phase.
11. The article of Claim 1, wherein the article is a medical device.
12. The article of Claim 1, wherein the medical device is a stent or a guide wire.
13. The article of Claim 1, wherein the medical device has a welded joint.
14. The article of Claim 1, wherein the medical device has a weld.
15. The article of Claim 1, wherein the article comprises an orthodontic arch wire, a dental implant, an orthopedic device or an eyewear frame.
16. The article of Claim 15, wherein the orthopedic device is used in bone.
17. The article of Claim 15, wherein the orthopedic device is used in the hip, knees, shoulder, elbows, or spine.
18. The article of Claim 1, wherein the article comprises at least a portion of a golf club.
19. The article of Claim 18, wherein the article is welded or brazed to the golf club.
20. The article of Claim 1, wherein the article comprises a golf club head.
21. The article of Claim 1, wherein the article comprises an insert for a golf club head.
22. The article of Claim 21, wherein the insert is welded, brazed or mechanically inserted onto the golf club head.
23. The article of Claim 22, wherein the insert is held in the golf club head by a tight toleranced fit.
24. The article of Claim 1, wherein the article has a welded joint.

25. The article of Claim 1, wherein the article has a brazed joint.
26. The article of Claim 1, wherein the article further comprises a portion having linear elastic properties.
27. The article of Claim 1, wherein the article further comprises a polymeric coating.
28. An article manufactured from a composition comprising:

about 8.9 wt% molybdenum, about 3.03 wt% aluminum, about 1.95 wt% vanadium, about 3.86 wt% niobium, with the balance being titanium.
29. The article of Claim 28, wherein the article is a medical device.
30. The article of Claim 28, wherein the medical device is a stent, a catheter introducer, a dental implant, a guide wire, an orthodontic arch wire, an orthopedic device used in bones or tissue, or an eyewear frame.
31. The article of Claim 28, wherein the article comprises at least a portion of a golf club.
32. The article of Claim 28, wherein the article comprises a golf club head.
33. The article of Claim 28, wherein the article comprises an insert for a golf club head and further wherein the insert is welded or brazed to the golf club head.
34. The article of Claim 28, wherein the article has a welded joint.
35. The article of Claim 28, wherein the article has a soldered joint.
36. The article of Claim 28, wherein the article further comprises a portion having linear elastic properties.
37. The article of Claim 28, wherein the article further comprises a portion having pseudoelastic or superelastic properties.

38. The article of Claim 28, wherein the article further comprises a polymeric coating.

39. An article manufactured from a composition comprising:

about 9.34 wt% molybdenum, about 3.01 wt% aluminum, about 1.95 wt% vanadium, about 3.79 wt% niobium, with the balance being titanium.

40. The article of Claim 39, wherein the medical device is a stent, a guide wire, a dental implant, an orthodontic arch wire, an orthopedic device for bone and/or tissue, or an eyewear frame.

41. An article manufactured by a method comprising:

forming a shape from a composition comprising titanium; and

a molybdenum equivalent weight of about 7 to about 11 wt%, wherein the weight percents are based upon the total weight of the alloy composition, wherein the composition is superelastic and/or pseudoelastic;

cold working the shape; and

solution treating the shape.

42. The method of Claim 41, wherein the solution treating is conducted at a temperature below the β transus temperature for the composition.

43. The method of Claim 41, wherein the solution treating is conducted at a temperature above the β transus temperature for the composition.

44. The method of Claim 43, wherein the shape is further cooled in air or in an inert gas.

45. The method of Claim 41, wherein the shape is further heat aged at a temperature of about 350 to about 550°C.

46. The method of Claim 41, wherein the heat ageing is conducted for a time period of 10 seconds to about 8 hours.

47. An article manufactured by a method comprising:

cold working a wire, wherein the wire has a composition comprising titanium; and a molybdenum equivalent weight of about 7 to about 11 wt%, wherein the weight percents are based upon the total weight of the alloy composition; and wherein the molybdenum equivalent weights are determined by the equation (1)

$$\text{Mo}_{\text{eq.}} = 1.00\text{Mo} + 0.28\text{Nb} + 0.22\text{Ta} + 0.67\text{V} + 1.43\text{Co} + 1.60\text{Cr} + 0.77\text{Cu} + 2.90\text{Fe} + 1.54\text{Mn} + 1.11\text{Ni} + 0.44\text{W} - 1.00\text{Al} \quad (1)$$

or the equation (2)

$$\text{Mo}_{\text{eq.}} = 1.00\text{Mo} + 0.28\text{Nb} + 0.22\text{Ta} + 0.67\text{V} + 1.43\text{Co} + 1.60\text{Cr} + 0.77\text{Cu} + 2.90\text{Fe} + 1.54\text{Mn} + 1.11\text{Ni} + 0.44\text{W} + 0.25(\text{Sn} + \text{Zr} + \text{Hf}) - 1.00\text{Al} \quad (2)$$

wherein Mo is molybdenum, Nb is niobium, Ta is tantalum, V is vanadium, Co is cobalt, Cr is chromium, Cu is copper, Fe is iron, Mn is manganese, Ni is nickel, W is tungsten, Al is aluminum, Sn is tin, Zr is zirconium and Hf is hafnium; wherein the aluminum can be substituted by carbon, boron, germanium and/or gallium; and wherein the respective chemical symbols represent the amounts of the respective elements in weight percent based on the total weight of the alloy composition.

48. The article of Claim 47, wherein the wire diameter is about 0.1 to about 10 millimeters.

49. The article of Claim 47, wherein the article has a martensitic structure.

50. The article of Claim 47, wherein the article has an elastic recovery of greater than or equal to about 75% of the applied change in length when the applied change in length is 2% of the original length.

51. The article of Claim 47, wherein the article has an elastic recovery of greater than or equal to about 50% of the applied change in length when the applied change in length is 4% of the original length.

52. The article of Claim 47, wherein the article is a medical device.

53. The article of Claim 52, wherein the medical device is a stent, a dental implant, a guide wire, an orthodontic arch wire, an orthopedic device used in bone and/or tissue, or an eyewear frame.

54. The article of Claim 47, wherein the article is used as a file or a drill in dental applications.

55. The article of Claim 47, wherein the article comprises an insert for a golf club head and further wherein the insert is welded or brazed to the golf club head.

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FIG. 1

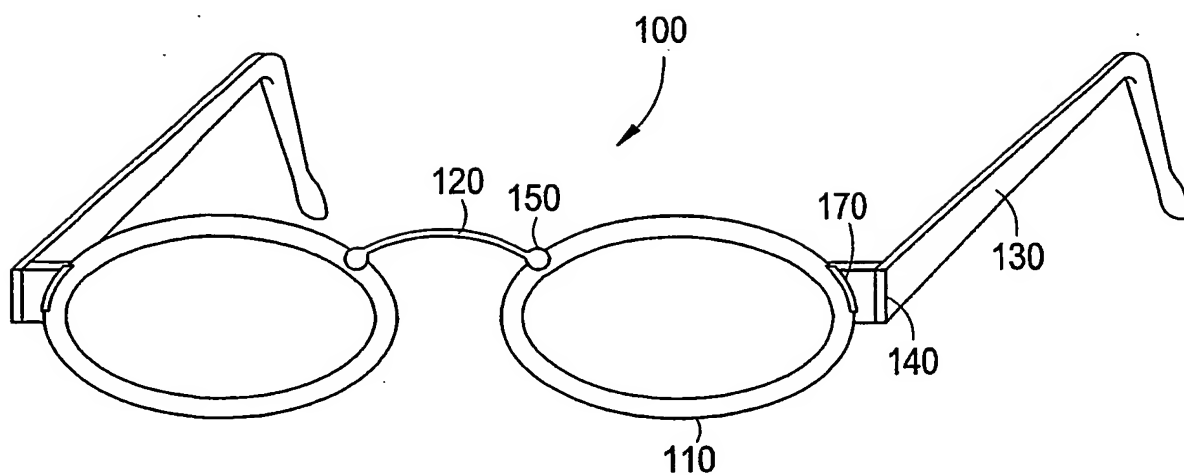
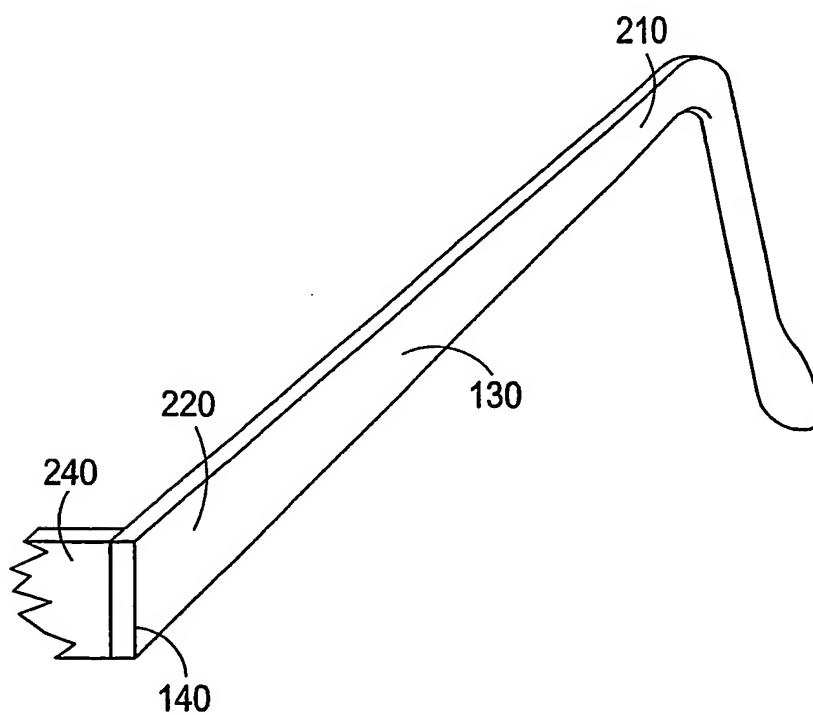


FIG. 2



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FIG. 3A

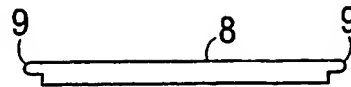


FIG. 3B

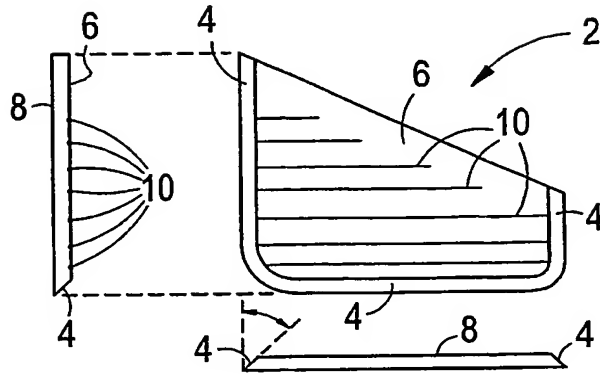


FIG. 4A

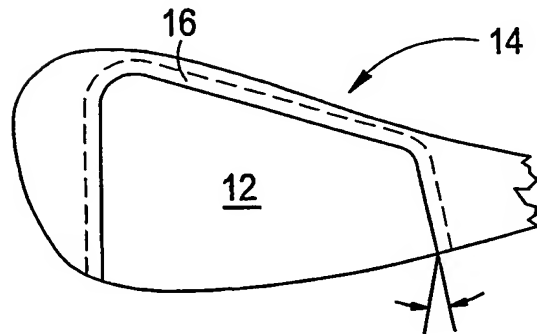


FIG. 4B

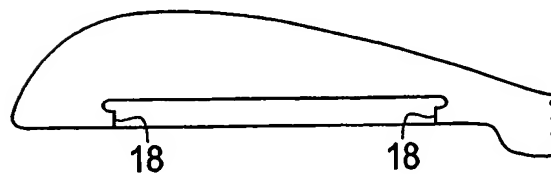
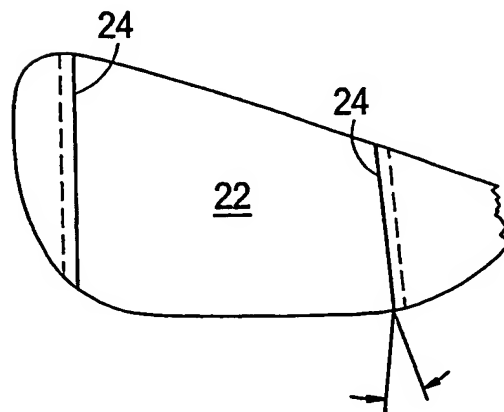


FIG. 5



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FIG. 6A

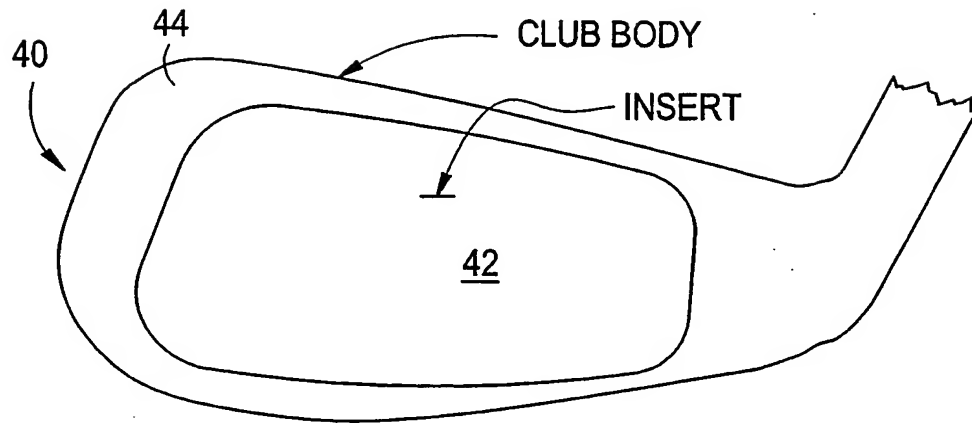
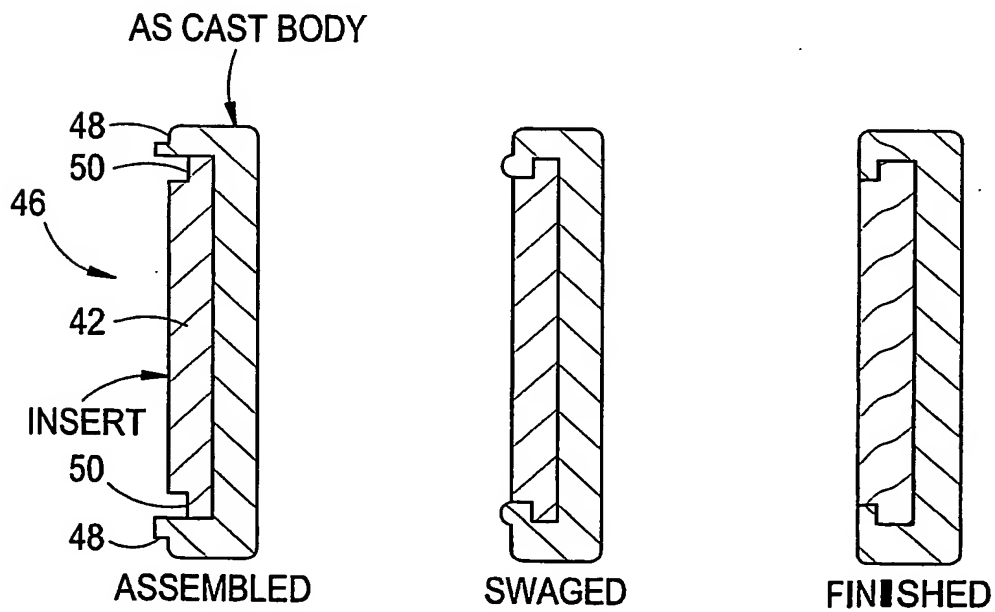


FIG. 6B

FIG. 6C

FIG. 6D



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FIG. 7

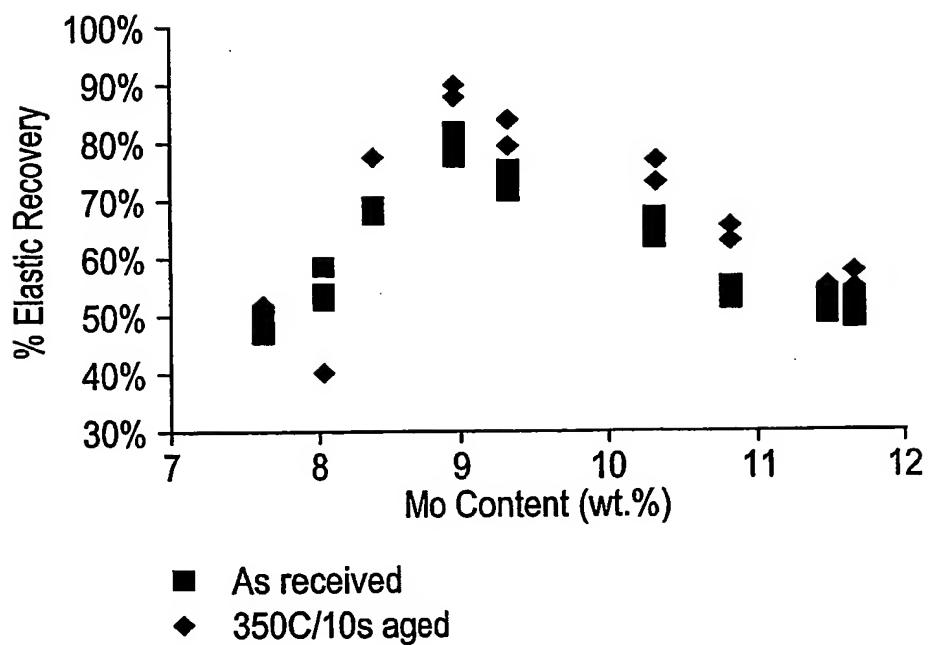
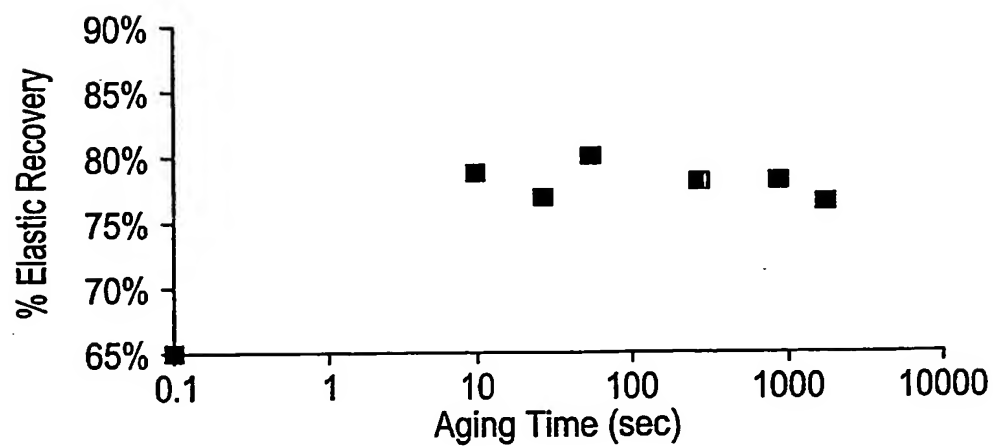


FIG. 8



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FIG. 9

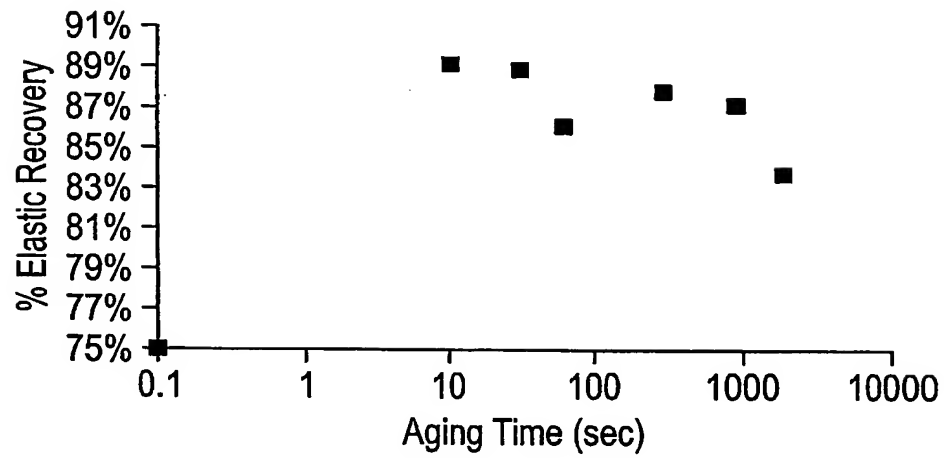
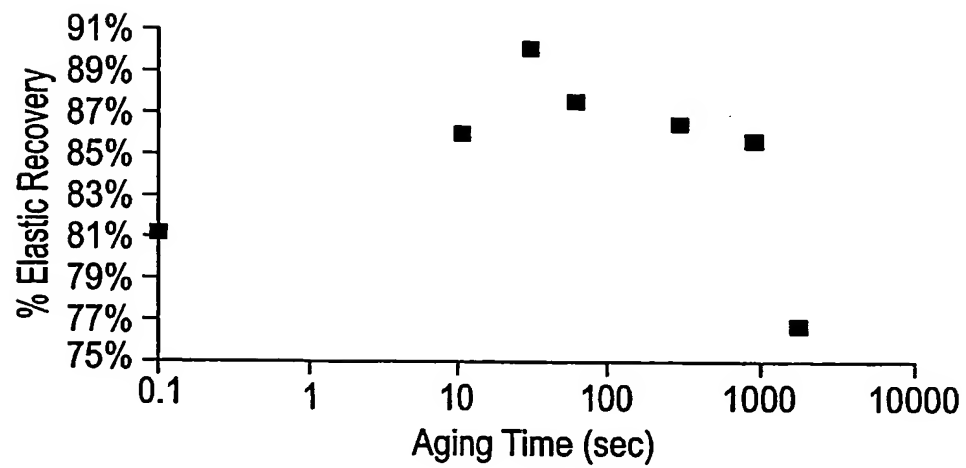


FIG. 10



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FIG. 11

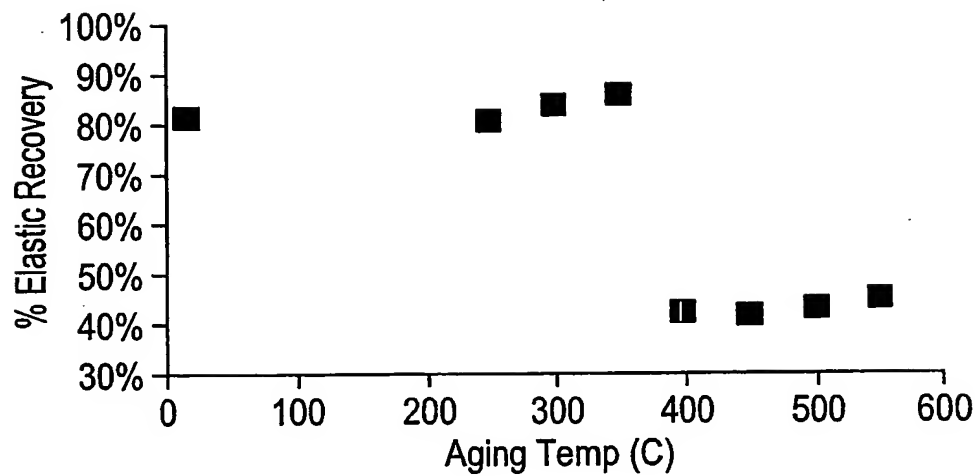
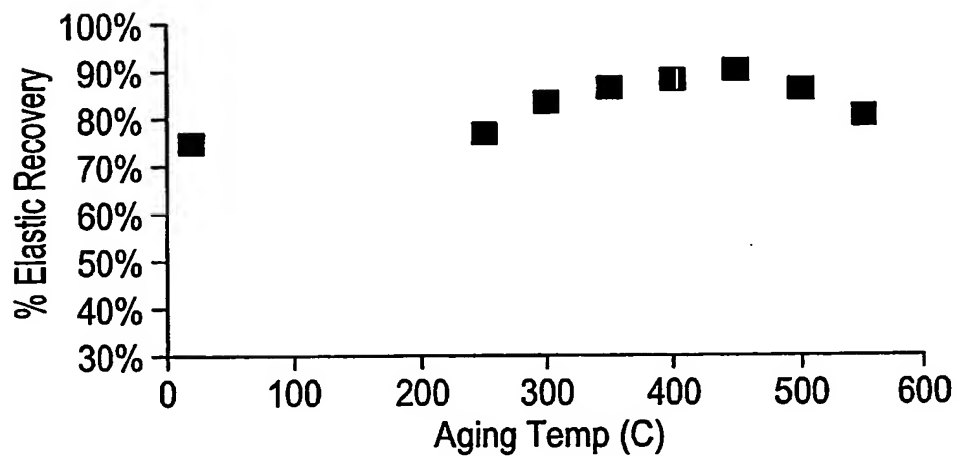


FIG. 12



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FIG. 13

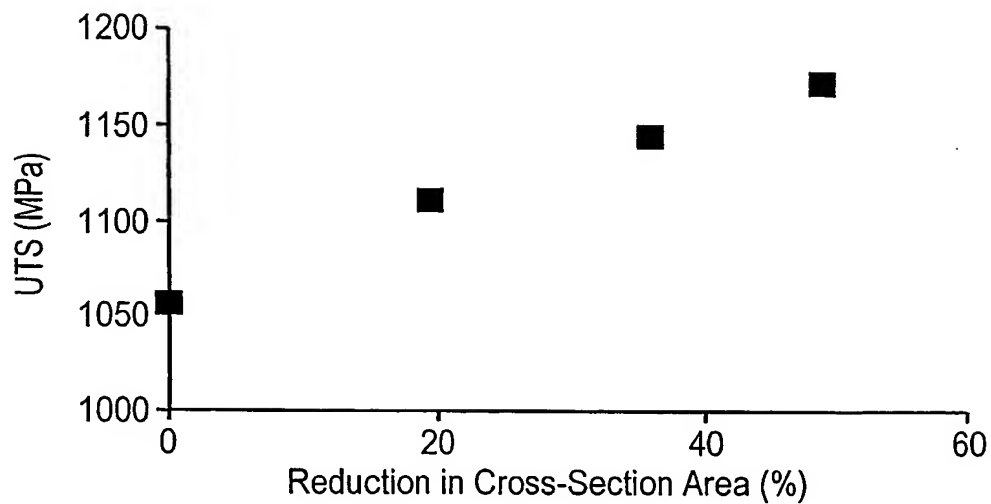
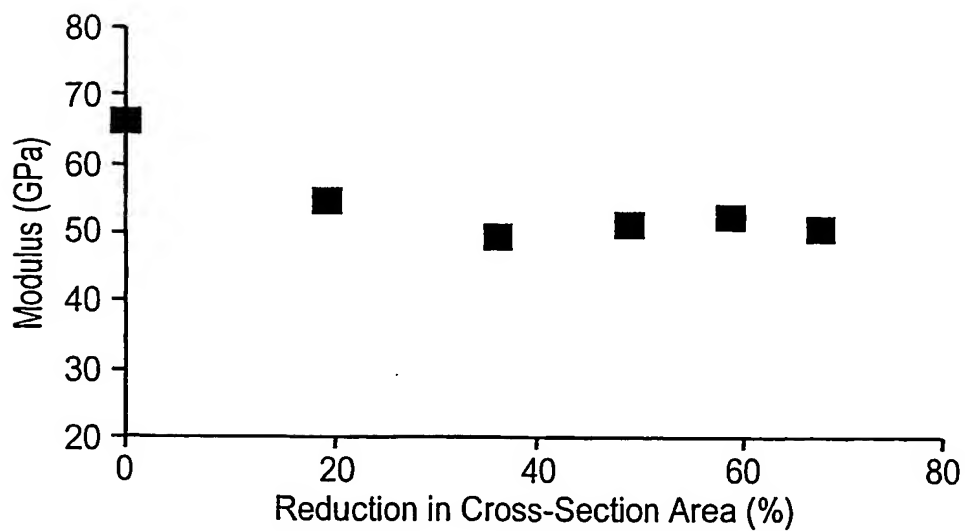


FIG. 14



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FIG. 15

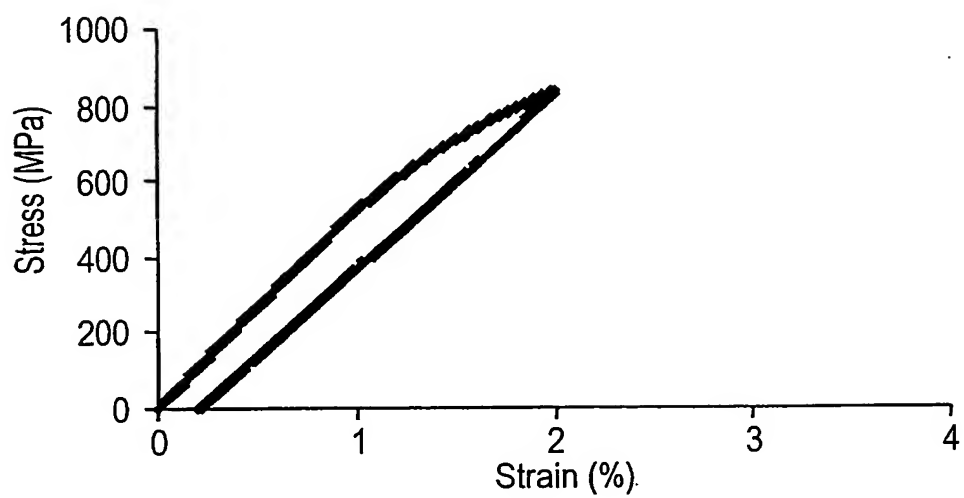
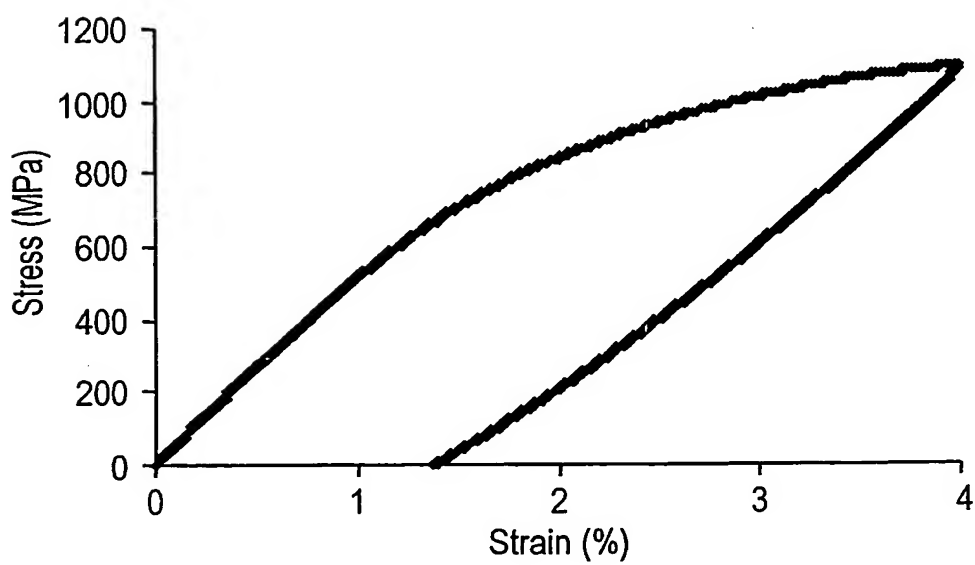


FIG. 16



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FIG. 17



FIG. 18



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FIG. 19

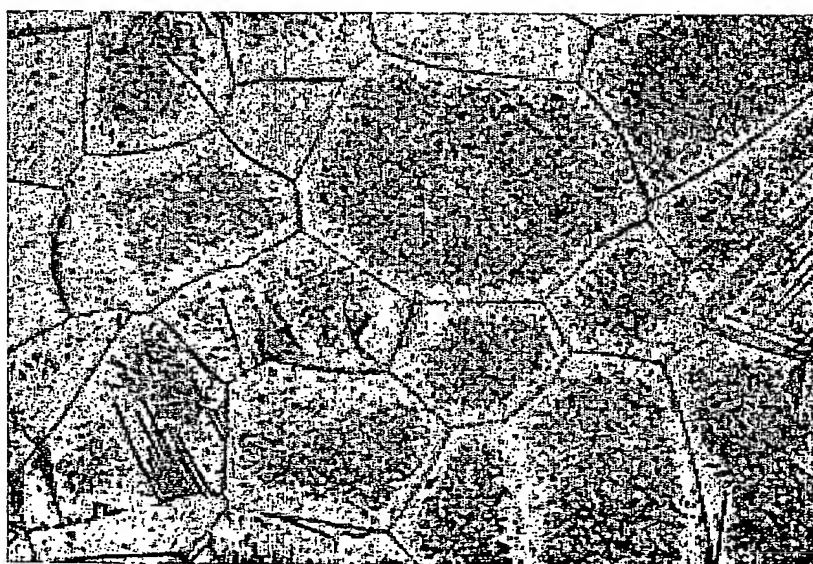


FIG. 20



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FIG. 21



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FIG. 22

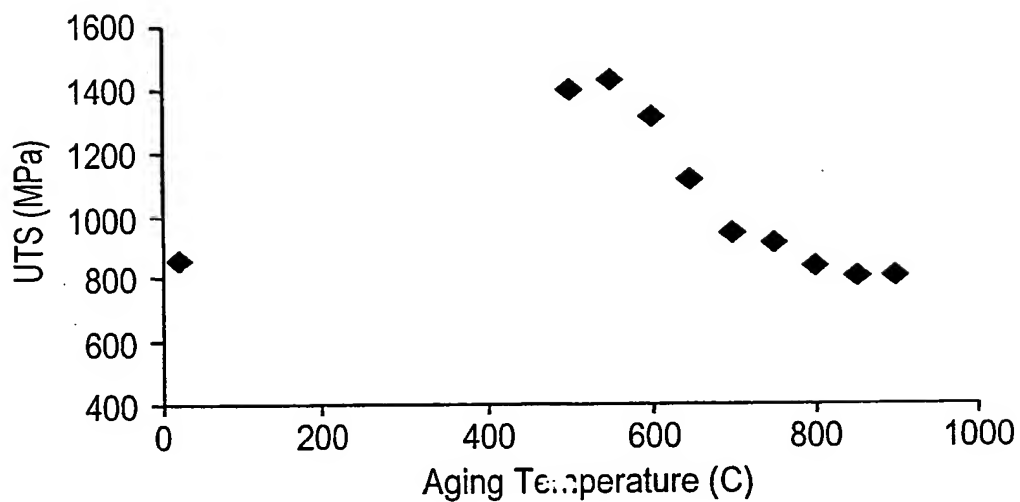
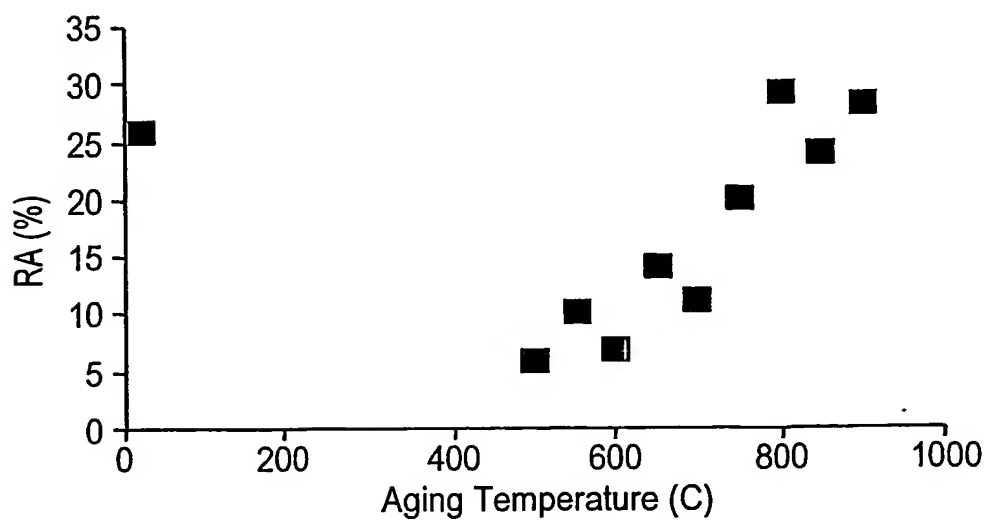


FIG. 23



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FIG. 24

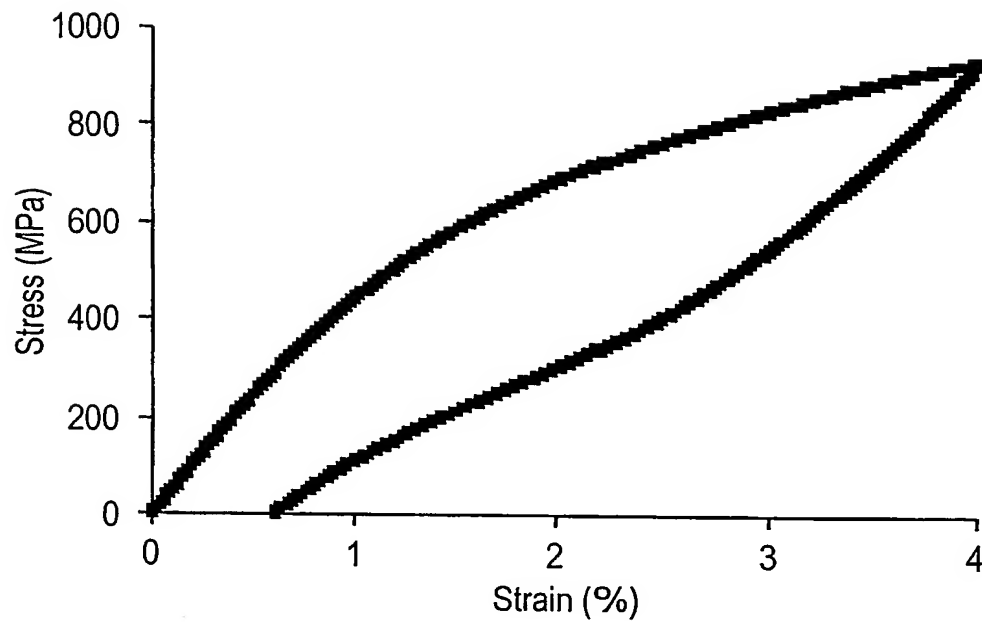


FIG. 25

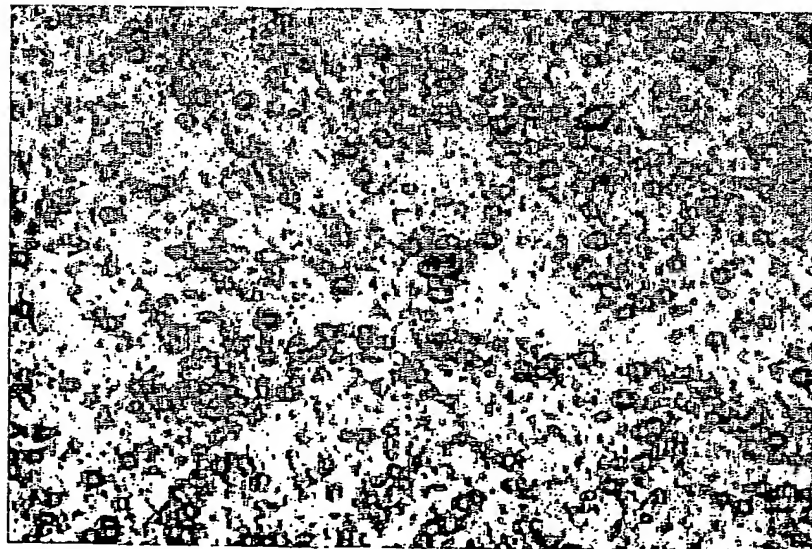


FIG. 26

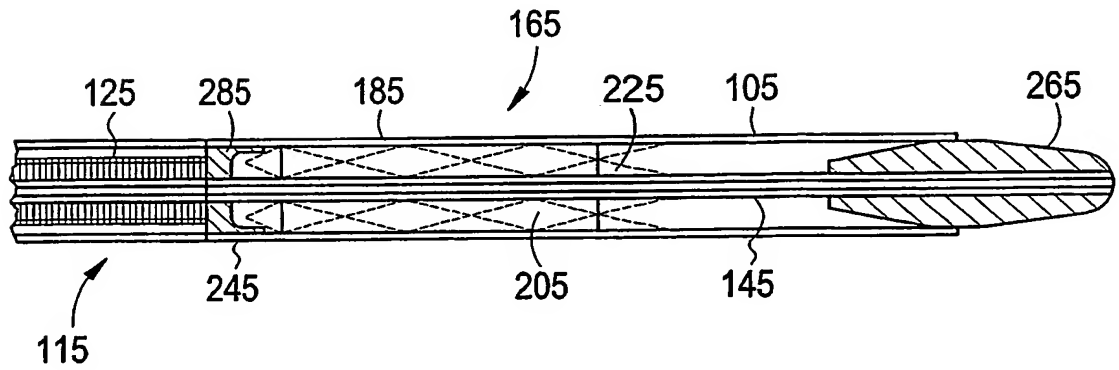
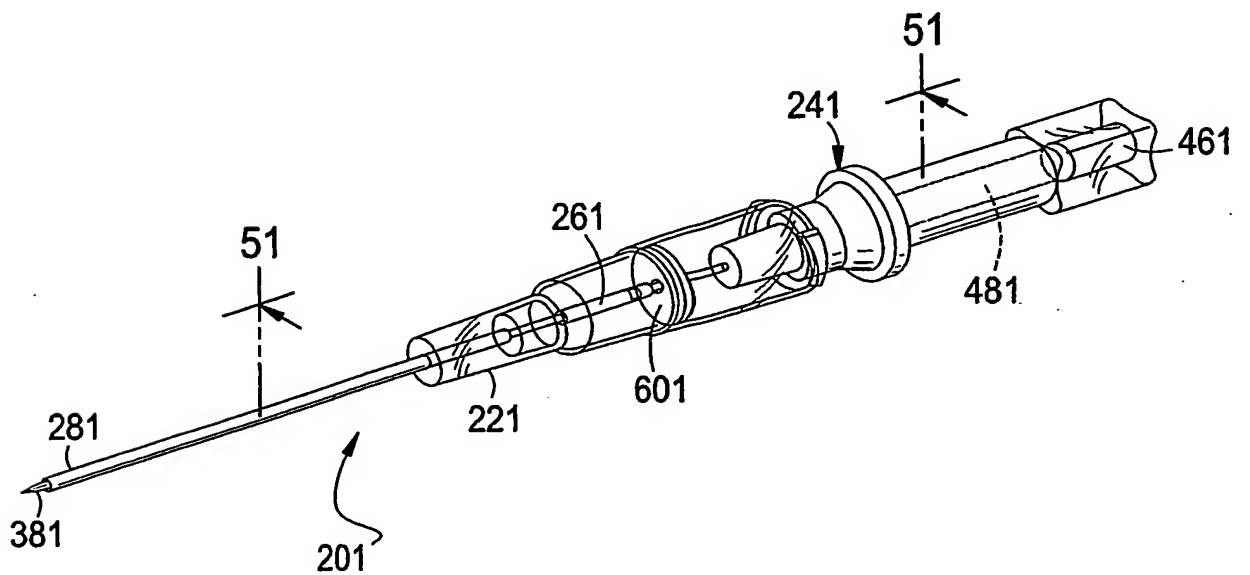


FIG. 27



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FIG. 28

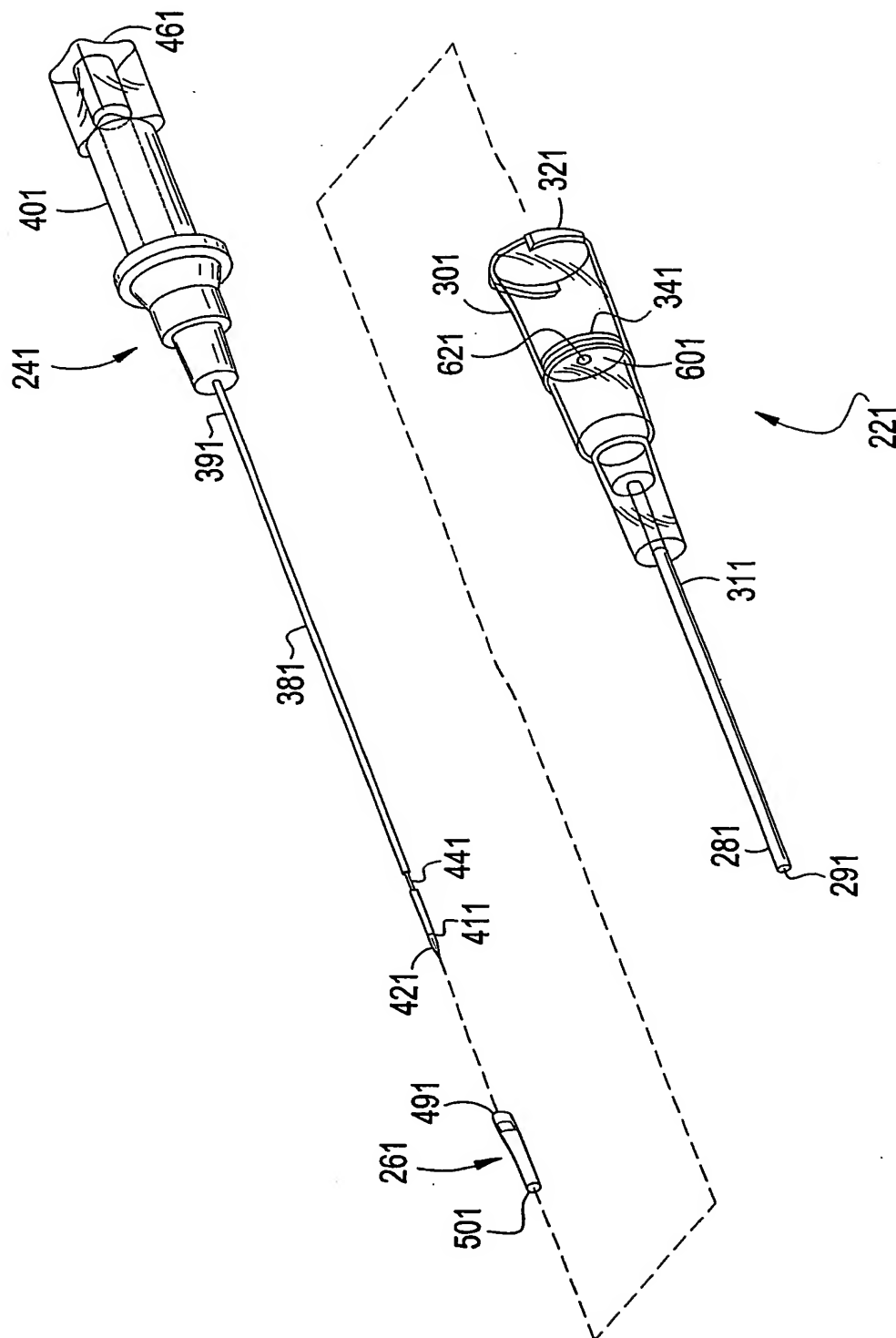


FIG. 29

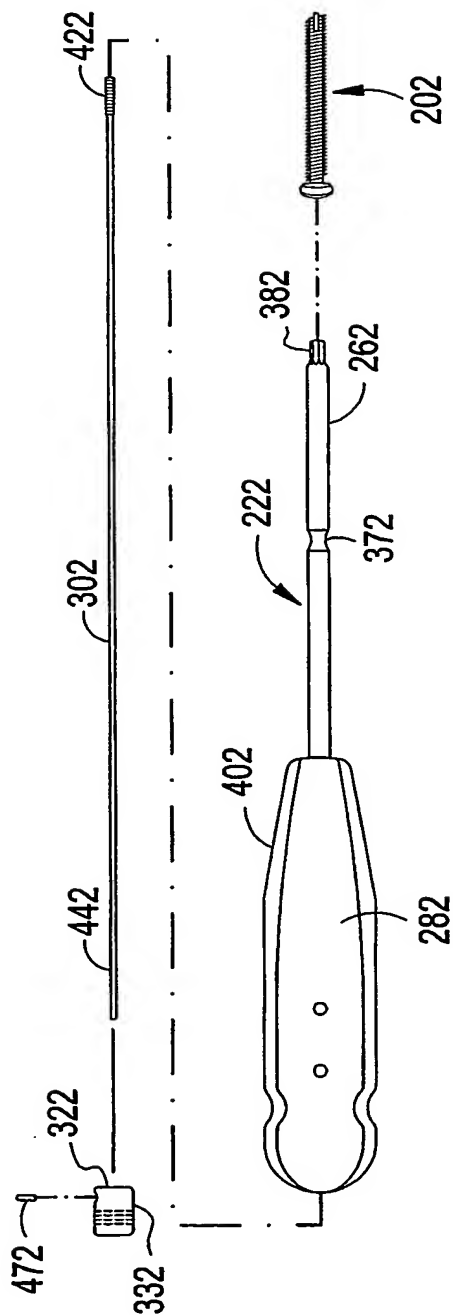
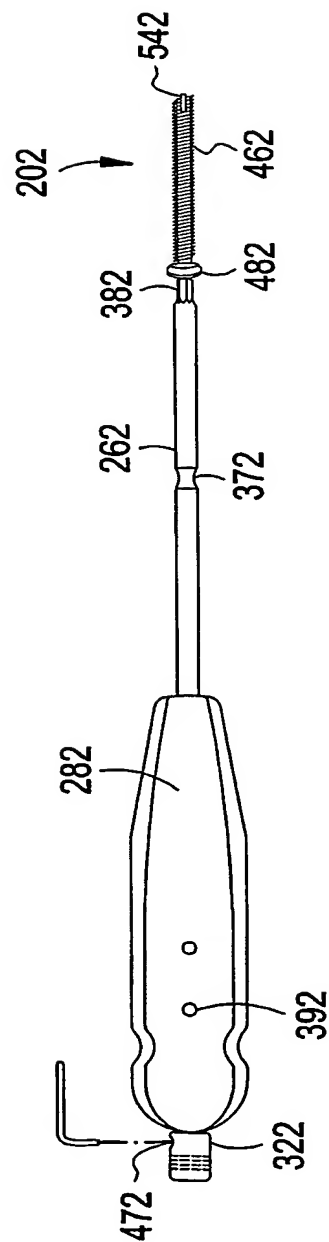
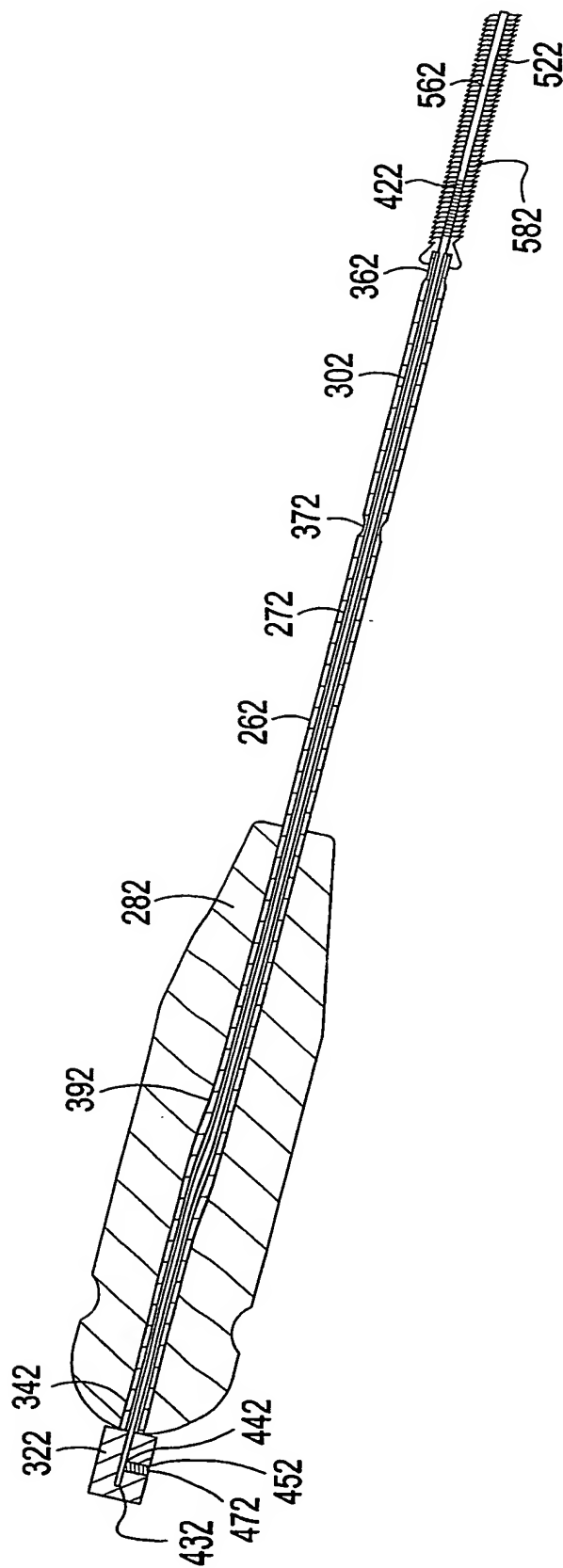


FIG. 30



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FIG. 31



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FIG. 32

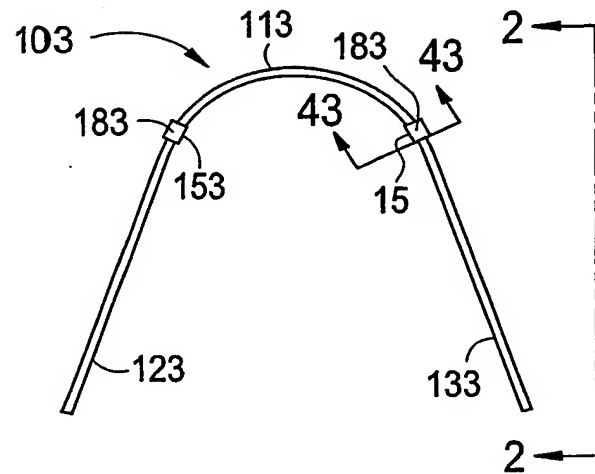


FIG. 33

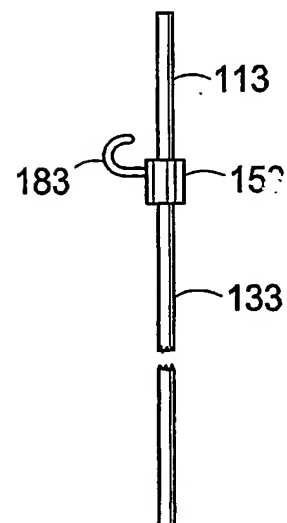
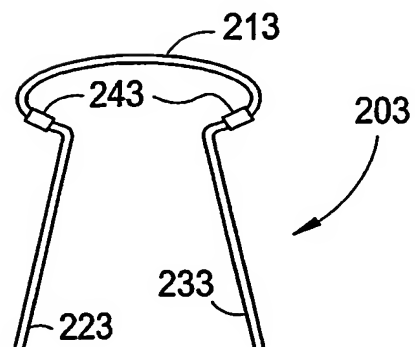


FIG. 34



A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22C14/00 C22F1/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22C C22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal; WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| P, X | WO 2004/003242 A (MEMRY CORPORATION) 8 January 2004 (2004-01-08) the whole document | 1-55 |
| X | WO 99/45161 A (MEMRY CORPORATION) 10 September 1999 (1999-09-10) the whole document | 1-55 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 August 2005

Date of mailing of the international search report

26/08/2005

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Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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Swiatek, R

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